

HANDBOOK OF NONFERROUS
METALLURGY

Edited by

DONALD M. LIDDELL

I. PRINCIPLES AND PROCESSES

II. RECOVERY OF THE METALS



Phoenix Metals U.S.A. II Inc.

ROBERT F. FLAHERTY
PRESIDENT

2816 Coast Line Court
Las Vegas, NV USA 89117

(702) 869-6181
Fax (702) 869-6286

Handbook of Nonferrous Metallurgy

RECOVERY OF THE METALS

PREPARED BY A STAFF OF SPECIALISTS

DONALD M. LIDDELL, Editor-in-chief

Metallurgical Engineer; Formerly Secretary of the Mining and Metallurgical Society of America; Formerly Managing Editor of the Engineering and Mining Journal; Author of "Metallurgists and Chemists' Handbook"; Editor of "Handbook of Chemical Engineering"; Coauthor of "Principles of Metallurgy"; Coauthor of "Mineral Resources of the United States and Its Capacity to Produce"; Lieutenant-Colonel, Air Reserve (Inactive)

SECOND EDITION
SECOND IMPRESSION

McGRAW-HILL BOOK COMPANY, Inc.

NEW YORK AND LONDON

1945

HANDBOOK OF NONFERROUS METALLURGY
RECOVERY OF THE METALS

COPYRIGHT, 1926, 1945, BY THE
MCGRAW-HILL BOOK COMPANY, INC.

PRINTED IN THE UNITED STATES OF AMERICA

*All rights reserved. This book, or
parts thereof, may not be reproduced
in any form without permission of
the publishers.*

THE MAPLE PRESS COMPANY, YORK, PA.

LIST OF CONTRIBUTORS

- R. G. Bowman.** General superintendent, International Smelting and Refining Co., East Chicago, Ind. *Lead.*
- Russel B. Caples.** B.S. Manager, Great Falls Reduction Department, Anaconda Copper Mining Co., Great Falls, Mont. *Electrolytic Zinc.*
- Stuart Croasdale** (deceased). *Chlorine Metallurgy.*
- H. A. Doerner.** B.S. Metallurgist, U.S. Bureau of Mines. Engineer in charge of metallurgical research at Pullman, Wash. *Ferroalloy Metals. Radium and Uranium.*
- Gordon I. Gould.** B.S. Engineer, H. W. Gould & Co. and New Idria Quick-silver Mine, Inc., San Francisco, Calif. *Mercury.*
- R. L. Hallett.** E.M. Mining and Metallurgical Engineer. Chief Chemist, National Lead Co., New York. *Tin.*
- E. A. Hersam.** B.S. Professor of Metallurgy Emeritus, University of California, Berkeley, Calif. *Manganese.*
- Walter Renton Ingalls.** Ph.D. Consulting engineer. Director, American Bureau of Metal Statistics, President, American Institute of Weights and Measures. *Cadmium, Zinc.*
- T. D. Jones.** Traveling lead refinery metallurgist, American Smelting & Refining Co., Perth Amboy, N.J. *Zinc-crust Treatment.*
- Frederick Laist.** B.Sc.; D.Sc. Vice-president in Charge of Metallurgical Operations, Anaconda Copper Mining Co., New York. *Electrolytic Zinc.*
- S. A. Laurich.** Chief chemist, Ferro Enamel Supply Co., Cleveland, Ohio. *Cobalt.*
- Donald M. Liddell.** B.A. Consulting chemical and metallurgical engineer; author; executive. Lt. Col., Air Res. (Inactive). *Editor-in-chief.*
- Alfred C. Loonam.** B.S. Consulting metallurgist, Deutsch and Loonam, New York. *Alkali and Alkaline-earth Metals.*
- M. J. Murphy.** Superintendent, Ferro Enamel Supply Co., Cleveland, Ohio. *Cobalt.*
- Enoch Perkins.** M.E. Vice-president, Mutual Chemical Company of America, New York. *Chromium.*
- Francis Pyne.** B.S. Engineer, WPB. Consulting Engineer, Elizabeth, N.J. Formerly manager, Raritan Copper Works. *Copper.*
- Gustave Reinberg.** M.E. Metallurgical engineer, Cerro de Pasco Copper Corp., New York. *Electrolytic Lead.*
- Guy C. Riddell.** B.S. Consulting engineer, mining and metallurgical industries (Engineers Club, New York). Consultant to Foreign Economic Administration, Washington, D.C. *Antimony.*
- R. B. Schaal.** Plant manager, Ferro Enamel Supply Co., Cleveland, Ohio. *Cobalt.*
- Walter C. Smith.** B.S. Metallurgist, Cerro de Pasco Copper Corp., New York. *Arsenic, Bismuth.*
- Henry A. Tobelmann.** B.S. Consulting engineer, Los Angeles, Calif. *Hydro-metallurgy of Copper.*

Elry J. Wagor. B.S. Superintendent, melting and refining department, U.S. Mint, Denver, Colo. *Refining of Gold and Silver Bullion.*

Chung Yu Wang. Ph.D. University medallist, Columbia University. Director of research, Wah Chang Trading Corp., New York. Technical expert, Ministry of Economic Affairs, China. *Antimony.*

Guy T. Wever. M.E. Superintendent of indium and rare metals department, Great Falls Reduction Department, Anaconda Copper Mining Co., Great Falls, Mont. *Electrolytic Zinc.*

PREFACE OF THE SECOND EDITION

THE improvements in the art of metallurgy have rendered a new edition of this handbook necessary, although it is to be regretted that certain information known to the contributors and to the Editor must remain unpublished because of security considerations.

In general, the plan of the first edition is repeated in the second. An attempt has been made to conform more closely to the idea of treating only of the reduction and refining of the metals and in the main to omit considerations of their working and utilization after production. This has resulted in the deletion of the chapter on Metallography and the addition of a chapter on Drying in its place.

Another departure from the general plan of the first edition is that each volume is indexed separately and it will be necessary to consult the indexes of both in order to make certain one has all the references to the subjects.

I wish to make special acknowledgement of the careful reading given the chapter on Aluminum by Mr. G. C. Riddell.

DONALD M. LIDDELL.

NEW YORK, N.Y.,
August, 1945.

PREFACE OF THE FIRST EDITION

THERE are certain processes and materials that are common to all metallurgical operations: the use of refractories, of fuels, general methods of concentration, of filtration, etc. It has been my attempt to pick out these metallurgical common factors and to give each of them treatment in a separate chapter, following these chapters with others describing the metallurgy of each metal; or, in some cases, two or more metals, when there is no basic difference in their metallurgy, are treated in one chapter.

The scheme of treatment in the various chapters is not uniform—it intentionally is not so. In general the attempt is made to treat at greatest length those metals of prime commercial importance, but this plan is departed from if it is felt that existing literature on a certain metal is not readily accessible to the ordinary metallurgical engineer. While with copper, lead and similar metals, the subject matter of the chapter is the extraction of the metal from the ore, in the case of such metals as magnesium and aluminum, where it is extremely unlikely that the average engineer will ever be called upon to design a reduction works, or to work in any plant except one with an established metallurgy, much of the space is given to the useful alloys of the metal and how to work with them. In some cases analytical methods are given when it is felt that existing literature is deficient.

There is much that is elementary. The book is designed for the student as well as for the engineer and consultant, yet it is hoped that there is enough advanced material to make the book useful to the metallurgist of experience, particularly if he is confronted with problems somewhat outside his own specialty. There is no attempt to give extensive tables of basic data—for these the seeker is referred to International Critical Tables, the tables of the International Congress of Applied Chemistry, or to Landolt, or to the editor's "Metallurgists' and Chemists' Handbook."

To the contributors is due more than their signed work indicates, as there has been much cooperative correction and criticism. I must, however, acknowledge special indebtedness to Percy E. Barbour, who took over all work on the book during my various absences from the United States during the period of its preparation, and also to H. A. Megraw and Dr. Colin G. Fink, who have given liberally of their time, and to Thomas A. Wright, of Lucius Pitkin & Co., for his hints regarding rare-metal recovery.

DONALD M. LIDDELL.

BALTIMORE, MD.,
May, 1926.

CONTENTS

	PAGE
PREFACE TO THE SECOND EDITION.	vii
*PREFACE TO THE FIRST EDITION.	ix
CHAPTER	
I. ALUMINUM (Liddell)	1
II. MAGNESIUM (Liddell)	44
BERYLLIUM (Liddell)	67
III. THE ALKALI AND ALKALINE EARTH METALS (Loonam)	73
IV. ARSENIC (Smith)	94
V. ANTIMONY (Riddell and Wang)	104
VI. BISMUTH (Smith)	139
VII. LEAD (Bowman)	144
VIII. TREATMENT OF ELECTROLYTIC SLIME AND ZINC CRUST (Jones)	216
IX. METALLURGY OF COPPER (Pyne)	227
X. REFINING OF GOLD AND SILVER BULLION (Wagor)	275
XI. HYDROMETALLURGY OF GOLD AND SILVER (Sharwood)	289
XII. HYDROMETALLURGY OF COPPER (Tobelmann)	345
XIII. ELECTROLYTIC REFINING OF LEAD (Reinberg)	370
XIV. THE ELECTROLYTIC ZINC PROCESS (Laist, Caples, and Wever)	379
XV. PYROMETALLURGY OF ZINC (Ingalls)	444
CADMIUM (Ingalls)	469
XVI. MERCURY (Gould)	473
XVII. THE ROLE OF CHLORINE IN METALLURGY (Croasdale)	517
XVIII. CHROMIUM (Perkins)	556
XIX. MANGANESE (Hersam)	566
XX. COBALT (Schaal, Murphy, and Laurich)	583
XXI. NICKEL (Liddell)	593
XXII. FERROALLOY METALS (Doerner)	615
XXIII. RADIUM AND URANIUM (Doerner)	637
XXIV. TIN (Hallett)	656
XXV. MINOR METALS (Liddell)	680
APPENDIX	707
INDEX	711

HANDBOOK OF NONFERROUS METALLURGY RECOVERY OF THE METALS

CHAPTER I

METALLURGY OF ALUMINUM AND ALUMINUM ALLOYS

BY ROBERT J. ANDERSON,¹ B. Sc. MET. E., D. Sc.

Introductory.—Aluminum is one of the lightest of the metals that are used in large quantities, having a specific gravity of $2.70 \pm$; once obtained as pig by modern reduction processes, it can be cast, worked, alloyed, and fabricated with moderate ease; metallurgically, it is one of the most interesting metals, but not one-tenth so much scientific investigation has been given to it as to iron. The merits of aluminum and aluminum alloys have been forced upon the engineering trades against a not inconsiderable opposition, and their worth as engineering materials has been proved beyond any doubt. Aluminum has established a place for itself among the nonferrous metals because of its intrinsic worth and, particularly, through its applicability to aircraft construction. Although aluminum is one of the most abundant metals of the earth's crust, it is at the same time one of the newest metals that have attained commercial importance.

Historical Survey.—Aluminum, as a metal, cannot lay claim to great antiquity, as contrasted with iron, copper, and the copper alloys, and it was a rare metal as late as 1850. Civilization is indebted to H. Sainte-Claire Deville for the pioneer work on reduction processes for the manufacture of metallic aluminum, but other investigators had carried out work prior to the eminent French chemist. Aluminum was first isolated by Oersted in 1825, who reduced aluminum chloride with potassium amalgam. The discovery of the metal has often been credited to Wöhler, who in 1827 reduced the chloride with potassium. Up to 1845, Wöhler had been able to produce only small amounts of aluminum, but still the amounts were sufficient to determine most of its properties. The attempts of early investigators to produce aluminum are described at length in some of the older texts (cf. Richards[2], Minet[3], *et al.*).²

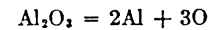
To H. Sainte-Claire Deville belongs the honor of having isolated aluminum in fairly large amounts in 1854. Deville first made aluminum by the reduction of aluminum chloride with potassium, and later improved the process, substituting the

¹ This chapter has been revised by the editor, 1944.

² Throughout this chapter reference numbers apply to the appended bibliography, except in the case of obvious footnotes.

cheaper sodium for potassium. Deville also perfected processes for the manufacture of sodium, which greatly reduced the price of both sodium and aluminum. The Deville processes, however, were all expensive and not adapted to the cheap production of aluminum in large tonnages. Aluminum was made in small amounts in France and England by the Deville-Castner sodium-reduction method until the invention of the Hall-Héroult process in 1886-1887, which drove all other processes from the field. In 1886, the Cowles process[12] calling for the reduction of alumina by carbon in the presence of a metal (*e.g.*, copper) in the electric furnace, was patented and used commercially. This was the first successful thermal process, but it yielded aluminum alloys and not aluminum.

In 1886, Hall in America and Héroult in Europe found independently that alumina dissolved in a liquid bath of aluminum fluoride and the fluoride of another metal yielded an electrolyte that would be decomposed by the electric current according to



The effect of the Hall-Héroult electrometallurgical method on the price of aluminum was felt soon after 1886, and all other processes were driven from the field by 1892. In 1855, the price of aluminum was \$113 per pound, in 1890 it was \$2.38, in 1900 it was 23 cents, and in 1920 the lowest price, 16½ cents, was reached, until the present war. In the interim from 1920 to 1939, the price varied from 20 to 33 cents.

Many workers have been associated with the rise of the aluminum industry. In addition to those mentioned above may be mentioned the names of Davy, Bunsen, the Tissier brothers, Webster, Grätzel, Kleiner, Moissan, Ruff, Guilini, Askenasy, Bradley, Winteler, Serpek, Doremus, Krause, Grabau, Frishmuth, Netto, Welden, and Richards.

Producers and Output.—The aluminum industry of the world has grown by leaps and bounds since the metal became relatively cheap commercially. In tonnage, aluminum now stands second among the nonferrous metals, and it is exceeded only by copper. The optimistic forecast that Dr. J. W. Richards made in the early years of this century, that the production of aluminum would overtake that of lead by 1930 and zinc by 1940, was not fulfilled, but it is interesting to note that in 1943 with a production of 1,840,358,000 lb. in the United States it passed both of these nonferrous metals.

Aluminum Ores and Bauxite Mining.—Aluminum is the most abundant of the commercial metals and is third in abundance of the elements in the earth's crust, following oxygen and silicon. Aluminum is nearly twice as abundant as iron, and constitutes about 7.85 per cent of the earth's crust (Clarke). Aluminum is an essential constituent of all important rocks, except the sandstones and limestones, but even in these its compounds are common impurities. Aluminum never occurs native, and, except for its fluorides, it invariably occurs as oxidized compounds. Thus, it is found mainly in the silicates, such as the clays, micas, and feldspars; as the oxide, corundum; as the hydroxide, bauxite; as the fluoride, in cryolite; and also in various phosphates and sulphates. Although aluminum minerals occur widely, few of these can be employed as ores in the manufacture of aluminum. Bauxite is the base ore for aluminum reduction and bears the same relation to aluminum that hematite does to iron. Cryolite, either natural or artificial, is the basis of the reduction-cell bath. The utilization of other materials will be discussed later in this chapter.

Bauxite and Related Minerals.—Theoretical bauxite has been given the formula $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, but the usual ore has a chemical composition midway between diasporite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; sometimes it is near the one and sometimes near the other. Bauxite is an earthy mineral and never crystallized; it occurs in a variety of forms, but usually has a pisolitic or oölitic structure, with rounded concretionary

grains embedded in a claylike mass. The color ranges from light cream through various shades of brown to a deep brownish red, depending on the iron content. Bauxite takes its name from the village of Les Baux, near Arles in France, where it was first found by Berthier. The following physical properties of bauxite may be noted as an aid to identifying the mineral: hardness, 1 to 3 (Mohs' scale); specific gravity, 2.55; melting point—on heating it changes to Al_2O_3 , which, when pure, melts at 1880 to 2050°C.; index of refraction, 1.57; color, white, cream, yellow, brown, gray,



FIG. 1.—Microstructure of bauxite pisolite with oölitic matrix; $\times 11$. (Shearer.)

or red; streak, variable; luster, dull to earthy; cleavage, irregular fracture; transparency opaque; tenacity, crumbly. Diasporite and gibbsite are associated with bauxite and found under the same conditions. Laterite is an aluminous ore, which is essentially a mixture of iron hydrate, aluminum hydrate, and silica in varying proportions. The Indian aluminum ores are laterites. Figure 1 shows the microstructure of a hard, high-grade, pisolitic bauxite from Georgia.

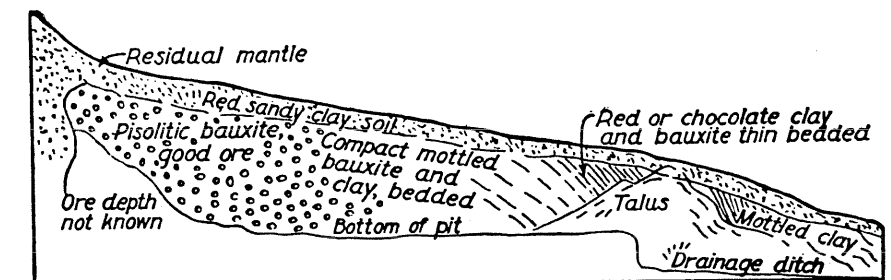


FIG. 2.—Typical bauxite deposit. (Hayes.)

Various theories have been advanced by geologists to account for the deposition of bauxite in the earth's crust. Bauxite occurs under a variety of conditions that suggest dissimilarity of origin, and no one theory appears to account for all cases. Figure 2 shows a section of a typical bauxite deposit. The theory of deposition has been discussed by Hayes[15] among others.

Commercial Bauxites.—Bauxite occurs at a number of places in the world, but high-grade deposits are not numerous, and it appears that known bauxite reserves

have a lower ratio to annual use than have the ores of any other common metal. Commercial bauxite ore is a hydrated oxide of aluminum, or a mixture composed of at least two and probably three hydrates, mixed with various impurities, chiefly iron oxide, silica, clay, and titania. Other impurities present are calcium oxide, magnesia, potassium oxide, and sodium oxide, in subordinate amount. The water content, both mechanical and combined, is variable over a wide range. Table 1 gives the chemical composition of some bauxites from various sources, which will serve to indicate the range of a variety of deposits. The color of bauxites varies considerably depending upon the iron-oxide content, being whitish when silica is predominant and red when

TABLE 1.—ANALYSES OF SOME BAUXITES FROM VARIOUS SOURCES¹

Source	Chemical composition, constituents per cent						
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Loss on ignition	Other constituents	Total
United States:							
Arkansas*	10.0	4.0	52.0	4.0	30.0		100.00
Arkansas*	4.0	4.0	53.0	10.0	29.0		100.00
Alabama*	2.10	3.12	61.0	2.20	31.58		100.00
Alabama	21.03	2.52	48.02	2.19	23.86	P ₂ O ₅ , trace	98.57
Georgia	6.62	1.05	64.91	0.28	33.53		100.89
Georgia	9.03	3.44	57.28	0.96	29.12		99.88
Austria:							
Sonntal	6.32	0.91	64.05	15.93	13.28		100.49
Feistritz	13.60	57.25	0.97	24.38	CaO, 1.80; P ₂ O ₅ , 1.40	99.40
Croatia:							
Rudopolje	6.30	66.02	14.82	12.70		99.84
Grgienbrieg	10.29	50.61	26.89	11.29		99.08
Dalmatia:							
Moséc	0.87	59.27	24.36	15.93		100.43
Ilvar	30.47	29.05	16.24	17.14	CaO, 6.79; MgO, trace	99.69
France:							
Var	0.30	3.40	69.30	12.90	14.10		100.00
Bouches-du-Rhône	4.80	3.20	55.40	24.80	11.60		100.00
Germany:							
Garbenteich	1.10	3.20	50.92	15.70	23.60	CaO, 0.80; MgO, 0.16	100.58
Firnewald	4.92	2.80	53.10	10.62	27.80	CaO, 2.62; MgO, trace	99.86
Hungary:							
Bihárhégység	6.69	3.10	58.70	19.23	11.80	CaO, 0.80	100.32
Királyerdő	1.62	1.15	60.83	25.82	11.31		100.73
Ireland:							
Antrim	6.01	61.89	1.96	27.82		97.98
Antrim	15.05	43.44	2.11	35.70		96.30

* Approximate composition.

¹ From different published analyses.

iron oxide is present in important amount. In a general way, the range of composition of bauxites is as follows: alumina, 55 to 65; silica, 5 to 30; ferric oxide, 1 to 25; and loss on ignition, 12 to 40 per cent. About 3 per cent of titania is associated with these oxides, and this is characteristic. Bauxites may be roughly classified, on the basis of their impurities, as follows: (1) high in iron and low in silica (red varieties); (2) low in iron and high in silica (white and gray); and (3) iron and silica contents about the same, either high or low. Bauxite is graded according to chemical composition, and sold to the consuming industries on the basis of chemical analysis. The grading and the marketing of bauxite have been discussed by Hill[31] and Ladoo[44].

Bauxites are used for abrasives, for chemical and refractory manufacture, and for the preparation of high-alumina cements, as well as for aluminum reduction; the grade of ore required is variable, depending upon the use. For different uses, the grades of bauxite desired in American practice are as follows:

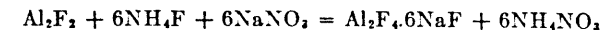
For aluminum manufacture: alumina, Al₂O₃, more than 52 per cent; silica, SiO₂, less than 4.5 per cent; and ferric oxide, Fe₂O₃, less than 6.5 per cent. (At the present time, bauxite, carrying less than 50 per cent Al₂O₃ and up to 15 per cent SiO₂, is being used.) High-grade bauxites for aluminum manufacture sometimes contain 58 to 65 per cent Al₂O₃, as little as 1 per cent Fe₂O₃, and 3 to 5 per cent SiO₂.

For chemical purposes (alum and aluminum sulphate preparation): alumina, Al₂O₃, more than 52 per cent; low ferric oxide and titania are preferable, *e.g.*, less than 3 per cent of each, but for some uses less pure ores are employed; requirements on silica are not set, but bauxites containing up to 19 per cent SiO₂ are used. It is definitely required that the alumina shall go readily into solution in dilute sulphuric acid.

For abrasives: various grades of bauxite are employed, but those low in iron and titanium are preferred. Generally, the requirements are: less than 5 per cent SiO₂, preferably 3 per cent; 2½ to 4 per cent TiO₂; and 3 to 5 per cent Fe₂O₃.

For refractories: the principal requirement is low iron and titanium contents, but the silica may be fairly high. So-called high-alumina clays, containing 48 to 52 per cent Al₂O₃, and high-grade diaspore, containing up to 80 per cent Al₂O₃, are now used in the refractory industry.

Cryolite.—Cryolite is an aluminum mineral of the composition Na₃AlF₆ (or 3NaF·AlF₃), required in the production of aluminum, being the chief constituent of the electrolytic bath and used to dissolve the alumina. The actual composition of pure cryolite is 32.8 per cent sodium, 12.8 per cent aluminum, and 54.4 per cent fluorine. The only commercial source of cryolite is the deposit at Ivigtut, Arakuford, South Greenland, owned by the Kryolith Mine & Handelsselskabet, A/S, of Copenhagen, Denmark. The high price of cryolite has led to the production of artificial cryolite, and this is now used generally in aluminum manufacture. Methods of preparation for artificial cryolite are described by Pattison[4], Mortimer[8], and others. In the Howard process,¹ the artificial product is prepared by the interaction of aluminum fluoride and sodium nitrate in the presence of ammonium fluoride, according to



In the Hulin process, pure hydrated alumina is treated with hydrofluoric acid, and the resulting product is saturated with sodium dioxide, giving artificial cryolite. Doremus also leached aluminous material with hydrofluoric acid.

Other Aluminum Minerals.—A few other aluminum minerals may be mentioned. Alunite, K₂O·3Al₂O₃·4SO₃·6H₂O, is a hydrous sulphate of aluminum and potassium, found in many places, and worked at Tolfa, Italy, and in Utah and Colorado. Alunite has been studied considerably as a source of both alumina and potash. Corundum is the sesquioxide of aluminum (Al₂O₃). It does not occur in sufficiently large deposits to make it an ore, but it was formerly used in the Cowles process for manufacturing aluminum alloys. The feldspars are an important group of rock-forming minerals containing aluminum, and some experimental work is being done on them as sources of alumina. The feldspars vary widely in composition and include such minerals as orthoclase, KAlSi₃O₈, and anorthite, CaAl₂Si₂O₈. Labradorite, a feldspar, found in large quantities in Norway, has been used experimentally as a source of alumina for aluminum manufacture. Leucite, potassium-aluminum

¹ U. S. patents, 1511560 and 1511561, Oct. 14, 1924.

metasilicate, $KAl(SiO_3)_2$, has been employed as a source of both alumina and potash. The well-known china clay, kaolinite, is a basic orthosilicate of aluminum, corresponding to $H_4Al_2Si_2O_7$, and is one of the most important minerals of aluminum. The mineral kaolin is known variously as white china clay, pure white clay, and fuller's earth. The great purity of high-grade kaolin and the large available deposits stamp it as the logical ore for the manufacture of aluminum, but it cannot be now employed because of the cost of separating the alumina from the silica. Common clays are simply very impure kaolins. Sillimanite, cyanite, and andalusite are three aluminum minerals of great importance to the ceramic industry because of their conversion on firing to a compound known as mullite or artificial sillimanite, which latter possesses very useful properties. The formula for sillimanite, cyanite, and andalusite is $Al_2O_3 \cdot SiO_2$. There are many other aluminum-bearing minerals, including some of our prized gems.

Bauxite Mining and Preparation.—Bauxite is mined ordinarily by open-pit methods, since the producing bodies are near the surface. Ladoo[44] has discussed the mining operations of the American Bauxite Co., in Arkansas, which are typical of large-scale production. The ore bed at Bauxite, Saline County, runs about 11 ft. thick, and the overburden is 25 to 140 ft. thick. In mining, the overburden is first stripped off by steam shovel, and the stripped surface is then cleaned and swept. The ore is loosely consolidated, but it is usually too hard to be mined without blasting. Low-strength dynamite is used for blasting. The loosened ore is loaded by steam shovel on cars. In the Georgia-Alabama-Tennessee district, the ore occurs in lenticular and irregular deposits which do not lend themselves to steam-shovel operation, and all mining is done by hand.

It should be pointed out that the concentration or beneficiation of loosely consolidated bauxite mixed with clay has been tried at a few mines in the United States, using log washers, but this practice is now rare here. In Germany, ores from many small concessions in Hesse were washed at a central washing plant. Recently, considerable interest has been displayed in the possibility of beneficiation of low-grade bauxites and bauxitic clays because of the dwindling of high-grade bauxite. Everhart has shown that clay can be separated from bauxite by washing in the presence of small amounts of added peptizers, *e.g.*, sodium hydroxide and the more strongly adsorbed sodium salts.

Bauxite, when mined, may be given preliminary treatment on the ground, depending on the nature of the ore. The bauxites found in the United States ordinarily contain 15 to 33 per cent combined water, together with a varying amount of mechanically held moisture, and, since the ores must ordinarily be shipped long distances, it is usual to dry the ore at the mines so as to save freight and to facilitate fine grinding for later use. For the preparation of alumina to be used in the manufacture of aluminum, bauxite is ordinarily crushed and dried at the mine, but not ground finely. In crushing, the crude ore is run through gyratory or other types of rock breakers and crushed to small nut size. Gyratory breakers are generally used for hard ores and disintegrators for soft ores. It is desirable to calcine most bauxites in order to remove organic matter which would interfere with the precipitation of aluminum hydroxide in the preparation of alumina, to oxidize ferrous oxide to ferric oxide, and to remove water which may be present in sufficient amount to form a pasty mass and clog the screens in fine grinding. For calcination, the ore may be heated at about $600^\circ C.$ in cylindrical rotary kilns of the type shown in Fig. 3. By such treatment, the moisture content is reduced to $\frac{1}{2}$ to 1 per cent. Kilns for calcination are 3 to 7 ft. in diameter and 30 to 100 ft. long.

The Bureau of Mines[78] has carried out some experiments on the flotation of bauxite. In its work it was found profitable to use either gravity or magnetic con-

centration for the removal of iron and titanium minerals, followed by flotation for the recovery of hydrated aluminum oxides and the rejection of the silica. To obtain a satisfactory separation between the hydrated aluminum oxides and the kaolinite, it is necessary to avoid floccules of finely divided bauxite and clay. Sodium hydroxide is the preferred dispersant. A pulp of 10 to 15 per cent solids gave the most satisfactory results. The most effective collectors for the hydrated aluminum oxides are oleic acid and fish-liver-oil fatty acid. The fatty resinous by-products of the paper-mill waste liquor are also fairly effective collectors, but they are more pronounced frothers. It would appear that if the bauxite were not crystalline in character there would be a heavy reagent loss, but the paper referred to does not touch on this phase of the process.

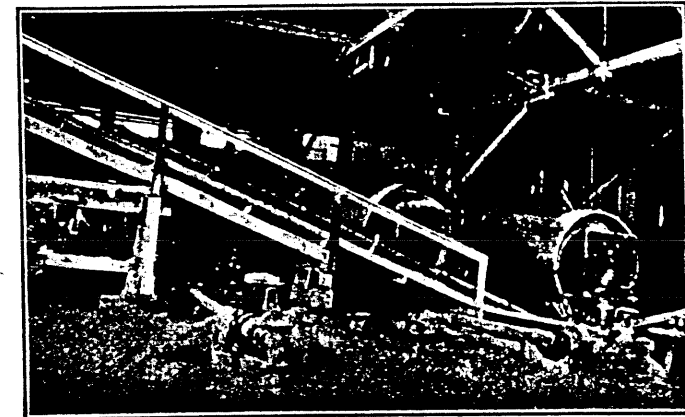


FIG. 3.—Rotary calcining kilns.

Production of Aluminum.—For the past fifty-five years, the production of metallic aluminum on a commercial scale has been carried out in two essential steps: (1) the preparation of alumina of high purity from bauxite, and (2) the electrolysis of the alumina in a liquid bath of cryolite plus other added salts. The reduction of alumina, Al_2O_3 , to aluminum cannot be done by carbon smelting, as with iron, copper, lead, and other commercial metals. Or, more precisely, alumina can actually be reduced by carbon, but, at the temperature and conditions of such reduction, the aluminum so reduced either volatilizes, oxidizes, or interacts with carbon monoxide or dioxide, forming aluminum carbide or aluminum oxide. Modern processes for aluminum reduction depend primarily on the preparation of substantially pure alumina, and this is the first step in the treatment of bauxite after calcination and grinding.

As pointed out previously, crude bauxite contains varying amounts of ferric oxide, silica, titania, and other impurities; these oxides must not be present in the alumina which is added to the electrolytic bath, otherwise the reduced metals, iron, silicon, etc., will appear in the resultant aluminum. It should be emphasized that one of the chief difficulties in the metallurgy of aluminum lies in the fact that the metal, after being produced, cannot be readily refined, as can copper and others of the commercial metals, and the purity of the metal secured by electrolytic dissociation depends primarily upon the purity of the alumina and the electrolytic bath. Many patents have been issued which apparently cover every conceivable method for obtaining aluminum from aluminum-bearing minerals, but the only commercial process is that one calling for the electrolytic dissociation of alumina dissolved in a liquid bath of cryolite plus other added salts. Electrolytic methods for the dissociation of

aluminum compounds are not applicable in aqueous solution, and fused electrolytes must be employed. For the electrolytic process, a primary requisite for commercial practice is a source of cheap electric current, since an enormous amount of current is required, and most of the aluminum-reduction plants in the world, except certain ones in Germany, consume electric energy derived from hydroelectric plants. For this reason, aluminum-reduction plants are normally situated within easy access of waterfalls, and steam-raised electric power is rare as a source of current for economical aluminum production.

Preparation of Alumina.—In the present Hall-Héroult process, the raw materials for the production of aluminum include substantially pure alumina, cryolite (plus calcium and aluminum fluorides for the bath), and carbon electrodes, and the first step in the manufacture of the metal consists in the purification of bauxite by chemical methods, whereby substantially pure alumina is produced. There are two main processes for the preparation of alumina, although many patents have been taken out for doing this in one way or another. These processes are (1) the Bayer process, and (2) the Deville-Pechiney process. The preparation of alumina has been discussed at length in the literature [2, 4, 8, 11, 30].

The usual process employed for the preparation of alumina from bauxite is the Bayer process, a wet chemical method. In this, the chemical principle involved is the formation of sodium aluminate by the treatment of bauxite with aqueous sodium hydroxide and the subsequent precipitation of aluminum hydroxide from the sodium aluminate, followed by calcination of the aluminum hydroxide to alumina, Al_2O_3 . In practice, calcined bauxite is first ground, *e.g.*, in a ball mill, to 100 mesh or finer, and this is next mixed with aqueous sodium hydroxide, specific gravity 1.45 (44.8°Bé.), in a vessel fitted with stirrers. After intimate stirring, the mixture is then run into steam-jacketed autoclaves and digested for 2 to 8 hr. under 50 to 70 lb. pressure at 150 to 160°C. The alumina of the bauxite is acted upon by the sodium hydroxide with the formation of sodium aluminate, according to



The impurities ferric oxide and titania are unaffected by the sodium hydroxide, as is the greater part of the silica. Part of the silica is dissolved and reacts with alumina and sodium oxide to form insoluble double aluminum sodium silicate. Dissolution of silica is prevented by adding lime to the bauxite during fine grinding, which forms insoluble calcium silicate and prevents loss of alumina. About 90 per cent of the alumina in the bauxite is dissolved by the digesting treatment.

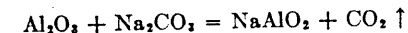
When the digesting treatment is completed, the liquor (including the residue of impurities) from the autoclaves is blown into large iron settling tanks of about 1600 cu. ft. capacity and allowed to settle for 4 to 5 hr. so as to effect separation of the solid impurities. The settled residue contains ferric oxide, silica, titania, and other impurities from the bauxite, as well as some alumina not dissolved, and is known as "red mud." This was formerly discarded, but some of it is now being reworked by the lime-soda sintering process, as a source of further alumina, and for titanium. The sodium aluminate liquor from the autoclaves is first diluted from specific gravity 1.45 to 1.23 (26.9°Bé.), and after settling in the tanks is run through filter presses for removing suspended matter and into large precipitation tanks or decomposing vessels. Figure 4 shows a type of tank fitted with stirring apparatus used by European producers[44] for precipitation of aluminum hydroxide. In precipitating aluminum hydroxide from the sodium-aluminate liquor, a small amount of freshly prepared aluminum hydroxide is added to the tank and the whole is stirred (the so-called "seeding" operation); aluminum hydroxide is precipitated from the liquor over a period of time running up to about 60 hr. About 70 per cent is precipitated in 36 hr.,

and the remainder precipitates on further standing. The precipitated aluminum hydroxide settles to the bottom of the tank, where it is drawn off and put through filter presses, yielding a product for calcination to alumina. The sodium-hydroxide liquor from the tanks is evaporated in vacuum pans and concentrated to specific gravity 1.45 for re-use in the treatment of raw bauxite.

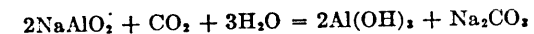
After filter pressing, the partially dried aluminum hydroxide is calcined so as to drive off water and yield substantially pure alumina. This calcination is generally carried out in tubular rotary kilns, lined with firebrick, and similar to those used in calcining bauxite or burning cement. The kilns are run at 1000 to 1100°C. The resulting alumina contains 98 to 99.5 per cent Al_2O_3 , and may contain up to 0.30 per cent mechanical water, 0.50 per cent combined water, 0.20 per cent silica, 0.10 per cent ferric oxide, and other impurities in subordinate amounts. After calcination, the alumina is ready for use in the electrolytic-reduction cell.

The Deville-Pechiney (or Le Châtelier-Morin) process was formerly the principal process for the preparation of alumina, but this has been largely supplanted by the Bayer process. The former is still used, however, for the treatment of bauxites especially high in iron and forms the basis of the so-called lime-soda sintering process for impure ores.

In the original process, ground bauxite, after calcination, is mixed with sodium carbonate, about 1 to 3 parts sodium carbonate and 1 part bauxite, and the mixture is roasted in a rotary or reverberatory furnace for 2 to 4 hr. at 1000 to 1100°C. A small amount of powdered coal is sometimes added to the mix. The sodium carbonate combines with the alumina, carbon dioxide is evolved, and the impurities are unattacked. The roasting must be done with care to avoid melting of the mix, and the product of the roast is a grayish-brown substance, consisting of a mixture of sodium aluminate and the impurities. The reaction is



After roasting, the mass is lixiviated with hot water, whereby the sodium aluminate is dissolved, while the silica, ferric oxide, and titania, being insoluble, are left as a residue. The liquor is settled for the removal of the solid impurities, as in the Bayer process, and is then passed through filter presses, for removal of any suspended matter, and then into tall precipitation tanks. For precipitation, carbon dioxide is blown into the liquor, and the reaction is



This precipitation requires 4 to 5 hr. and is carried out at 70°C. The precipitated aluminum hydroxide is filter pressed, dried, and calcined, as in the Bayer process, yielding alumina[76].

Some other processes have been devised and actually employed for the preparation of alumina, and will be discussed below. Certain other methods for obtaining a compound of aluminum (such as the fluoride, nitride, carbide, and chloride) from aluminum minerals have been worked out. A few of these possess potentialities, but the majority of them have no discernible commercial possibilities. While many processes have been devised for the preparation of alumina from clays and other

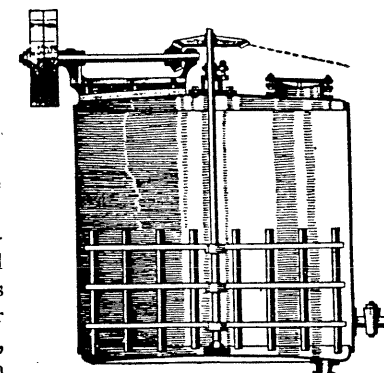


FIG. 4.—Bayer precipitation tank.

fairly high aluminous minerals, none of these had been commercial in the United States, under peacetime conditions, though some had a limited use abroad. A few processes that have been employed commercially or have reached the semicommercial scale are discussed briefly below.

Treatment of Low-grade Bauxites.—Partly owing to the dislocation of steamship communications and partly owing to an actual shortage of high-grade bauxite, a great deal of attention has been given in the last few years to the recovery of alumina from second-rate materials. Probably in the United States the largest amount of alumina recovered from low-grade materials has been by the so-called "lime-soda-sinter process," sometimes known as the "Deville process." In this process, the material is mixed with limestone and soda ash and calcined; the sintered mass is then leached with hot water for the extraction of the soluble alumina; the solution is treated in an autoclave at a temperature of 160°C. and 85 lb. pressure, under which condition the bulk of the silica forms insoluble sodium-aluminum silicate. After settling and filtering, the solution is treated with carbon dioxide for about 5 hr. at 70°C., to precipitate the alumina[72].

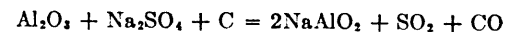
A variation of this lime-soda-sinter process has been tried at the Monolith Portland Midwest Co. pilot plant at Laramie, Wyo. At this plant an anorthosite has been substituted for bauxite and treated by the lime-soda-sinter process. The results at the pilot plant were so encouraging that the WPB authorized the erection of a semi-commercial plant and indicated that the pilot plant would be used to test the lime-soda-sinter process on clays.

Ammonium Sulphate Exchange Process.—In the best known of these processes a mixture of pulverized clays and ammonium sulphate is treated at temperatures of 373 to 400°C. in a rotary kiln, ammonia being evolved and ammonium aluminum sulphate being formed[71]. The reacted mass is then leached at 95 to 100°C. with water slightly acidulated with sulphuric acid and the solution separated from the insoluble residue. The ammonium aluminum sulphate is recovered by crystallization and after being redissolved is treated with the ammonia and ammonium carbonate (the last resulting from the mixture of ammonia with the combustion gases of the initial treatment).

Aluminum hydroxide is precipitated and filtered off, and the ammonium sulphate is recovered by crystallization for re-use with more clay or low-grade bauxite. The basic patents so far as the editor knows are the German patents of Hess (376717 and 388996) and of Riedel (386614).

The Buchner process is a variation of the ammonium sulphate process and is sometimes known as the "Aloton process." In this, clay is heated with acid ammonium sulphate at 200°C. In other particulars the process is the same as that of the preceding paragraphs.

Another variation of the sulphate decomposition is the Peniakoff process in which clay or bauxite and sodium sulphate are heated together with a little coal at 1200 to 1400°C.



Sulphuric Acid Process.—Practically all ammonium silicates can be decomposed with fair efficiency by sulphuric acid at temperatures in the neighborhood of 200°C. and with acids of about 1.25 specific gravity.

Sulphurous Acid Leaching.—This reagent has been experimented with for many years, the earliest patent on the subject being E. Raymond's U. S. patent 650763, taken out in 1902, and the latest known to the author being Goldschmidt's 2006851, taken out in 1935. The Goldschmidt process leaches with aqueous solutions of SO_2 under pressure at 60 to 80°C. Alumina and aluminum sulphite are precipitated on

release of pressure. The objections reported to the author are a tendency of iron to form soluble bisulphites and then to precipitate just as does the alumina, so that the precipitated alumina must be purified, and also the fact that the sulphur dioxide oxidizes to sulphur trioxide, resulting in a loss of the reagent.

Nitric Acid Process.—Nitric acid leaching has always been tried experimentally at temperatures in the neighborhood of 170°C. and 120 lb. pressure per square inch. The high cost of nitric acid and the loss of this reagent have prevented any commercial applications.

Hydrochloric Acid Leaching.—The best known of the hydrochloric acid processes is probably that of Chemische Fabrik Griesheim[73]. This is essentially a process to treat high-silica bauxites. The alumina and iron dissolve in hydrochloric acid, the solution being reduced after this treatment with sulphureted hydrogen. The solution is evaporated and heated to 300°C., which hydrolyzes the aluminum chloride in its own water of crystallization. If this temperature is not exceeded, the ferrous chloride is in the main water-soluble. However, it is reported that even with the most careful work, the alumina requires a cleanup with chlorine to free it from the last of the iron.

Dr. Arthur Hixson and Ralph Miller worked on a process for leaching roasted clay with concentrated hydrochloric acid[77], converting the aluminum and iron into soluble chlorides, but leaving the silica insoluble. The novelty in this process was the use of isopropyl ether to remove the ferric chloride from the solution. This could then be evaporated and the aluminum chloride hydrolyzed to give alumina and hydrochloric acid. The process required the circulation of one ton of isopropyl ether per ton of alumina recovered, and this was apparently the main reason for the National Academy of Sciences and the WPB refusing materials to give the process a trial. This need not be considered final proof that the process is unworkable.

Hydrofluoric Acid Leaching.—The use of hydrofluoric acid for leaching clays and low-grade bauxites has also been experimented with fairly extensively. The patents of Dr. Charles A. Doremus (723251 and 725683) are the oldest known to the author. Apparently the recovery of alumina was high, but there were heavy losses of the expensive reagent as insoluble fluosilicates and as silicon tetrafluoride.

Recovery from Alunite.—A number of processes have been used for the treatment of alunite, $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$; these were well summarized by Robert J. Anderson in the *Mining Magazine*, December, 1936, page 340. At the present time, a plant has been constructed near Salt Lake City to use the Kalunite process. The crude ore is crushed and given a dehydrating roast at 550°C., which renders it soluble in dilute sulphuric acid. The hot calcine is cooled to 200°C. and given a countercurrent agitation and leach in a solution of potassium sulphate and 10 per cent sulphuric acid. The countercurrent leach is operated to maintain an excess of roasted alunite in the first agitator so that the pregnant solution contains no free acid. This is an important step in eliminating impurities. The pregnant solution is filtered out and then cooled, normal potassium alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, crystallizing out. The alum crystals are washed, dissolved with dilute potassium sulphate solution, and treated in a continuous autoclave at a temperature of 200°C. The potassium alum is broken down into a basic alum, $\text{K}_2\text{SO}_4 \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, plus sulphuric acid and potassium sulphate. The acid and potassium sulphate are recycled for the original leach, and the basic alum is calcined at 1000°C. to decompose it into alumina and potassium sulphate. The calcine is then leached with hot water to remove the soluble potassium sulphate, leaving behind the alumina. The leach solution is then evaporated to crystallize out potassium sulphate[69, 70].

The Moffat process is essentially the same except that the alum recovered in the process is broken down by a flash roast.

In Italy both alunite and leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, have been used for the production of alumina and potash. The process used for the treatment of leucite is the Blanc process, which leaches with dilute sulphuric acid. It is reported that agitation cannot be used, as the silica gelatinizes when agitated and holds up much of the solution. It is claimed that if the leaching is done by straight percolation without agitation little trouble results from the silica.

Japan has probably produced much of its alumina by the following four methods and the Suzuki process described under Fusion Processes, below. In the Asada process, alunite is calcined at 600°C. and is treated with sulphuric acid and potassium sulphate. After filtering and cooling most of the aluminum salts out as alum. The mother liquor goes back to the solution cycle, and the potassium alum is decomposed into basic aluminum sulphate and acid potassium sulphate. (See page 11, discussion of Kalunite process, for details of further treatment.) In the Okazawa process (Showa potassium process), alunite, crushed and calcined at 600°C., is treated with potassium hydroxide. Potassium aluminate and sulphate go into solution, silica remaining behind. (See page 11, discussion of Kalunite process, for treatment of the sulphates.) In the Sumitomo process, alunite is leached with sulphuric acid. On cooling, alum and aluminum sulphate salt out and are filtered off, redissolved, and treated with ammonia, giving alumina as a precipitate and potassium and ammonium sulphates in solution. In the Tanaka process, alunite is calcined at 600°C., crushed, pulped with water, and treated with about 8 per cent its weight of ammonia. Potassium and ammonium sulphates are left in solution and are recovered for fertilizer use. The washed residue is treated with caustic soda (Bayer process). This is apparently the process sometimes described as the Showa sodium process.

Fusion Processes for Alumina Production.—Treatment of high-iron bauxite in the electric furnace has been practiced successfully on a commercial scale in Norway[71]. The Pederson process appears to be the one worked on by our own Bureau of Mines in a pilot plant to test the process. This should not be confused with the Pederson process that sinters clay with lime and subsequently leaches the melt with soda. This second Pederson process is of course a modification of the lime-soda-sinter process.

The Bureau of Mines reports that the only practical method of making calcium aluminate from high-silica bauxite is by a two-stage treatment. In the first stage, the silica and iron oxide are reduced to ferrosilicon. The molten slag from this operation, which contains 95 to 98 per cent alumina, is transferred to a second furnace where with the addition of lime monocalcium aluminate is produced. This compound is readily decomposed by sodium carbonate solution, producing a solution of sodium aluminate from which alumina can readily be recovered.

The Haglund process is also understood to have been in successful use in Scandinavia. In the original Haglund process, clay and pyrites were smelted, using a reducing agent to produce ferrosilicon and an aluminum sulphide slag, which was later hydrolyzed for the production of alumina. (Incidentally, this appears to be about the same as the old Halvorsen process.)

The later Haglund process reduced only about one-fifth of the alumina to aluminum sulphide. The mixture of aluminum sulphide and aluminum oxide gave a lower melting-point slag than that of the original process and also cut down the amount of ferrosilicon produced and marketed. In the newer process, as in the old, ferrosilicon was produced and formed a heavy layer under the slag. The slag was decomposed with water, and the sulphureted hydrogen that was generated was sold as such or was worked into sulphur for further use in the process.

The Suzuki process reduced clay with coke for the production of ferrosilicon, and the residual alumina was cleaned with chlorine at 500 to 600°C. A long discussion of this matter of purifying ferruginous alumina and bauxite was prepared by Dr. Colin G. Fink and V. S. de Marchi and published by the Electro-Chemical Society in its 1938

transactions, page 511. E. C. Eckel experimented at Mussel Shoals as early as 1934 on the treatment of low-grade bauxites carrying 30 per cent silica and 30 per cent iron sesquioxide[74]. From such a bauxite he produced ferrosilicon with a slag that carried less than 2 per cent silica and 1 per cent iron.

The Berger and Kuhne process smelted kaolin, clay, or bauxite with iron pyrites, magnesium chloride, and iron filings, aluminum chloride being distilled and condensed. The Miguet process fused clay, lime, and scrap iron with a reducing agent to produce ferrosilicon and calcium aluminate, but apparently these processes could not produce alumina in competition with the natural bauxite (see *U.S. Bureau of Mines Report of Investigations* 2393).

Loevenstein Process.—Of interest as an outstanding novelty is the process devised by Hirsch Loevenstein and operated on a pilot-plant scale in France by Jacques Fondal before the German invasion[77]. Clay is smelted in an electric furnace to a mixture of aluminum, silicon, iron, and impurities, and the product is treated in a bath of molten zinc. The aluminum only is soluble. The zinc is then distilled from the aluminum.

Serpek Process.—In the Serpek process, aluminum nitride is produced by heating ground bauxite and carbon in an atmosphere of nitrogen at 1600 to 1800°C. The aluminum nitride formed under these conditions can be decomposed with water.



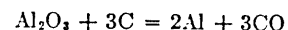
The plant of the Southern Aluminium Co. was originally intended to use this process, but never worked commercially on it.

Primary Aluminum Manufacture.—The present commercial process for the production of aluminum is essentially the same as that described in the original Hall-Héroult patents of 1886 to 1888, and all aluminum made today is produced by the electrolytic dissociation of alumina dissolved in a bath of liquid (fused) cryolite plus other added salts. The sodium-reduction process need not be considered here, since it is only of historical interest, but it is important to direct attention to the Cowles alloy process. It should be pointed out that, although Hall applied for his patents in 1886, these were not granted until 1889, and in 1886 Héroult also applied for a United States patent on essentially the same process as described by Hall. The essential differences in the patent applications were in the composition of the electrolyte and the design of the furnace, but the two processes are identical to all intents and purposes. When the separate discoveries of Hall and Héroult were made simultaneously, there was no patent litigation, but the Hall company took the American field and the Héroult company the European field.

The Cowles process[12] for the manufacture of aluminum alloys direct from Al_2O_3 was patented by A. H. and E. H. Cowles[13] in 1885, and plants for conducting the process were built at Lockport, N. Y., and Stoke-on-Trent, England. In essence, the Cowles process called for the reduction of alumina by carbon in the presence of a metal (e.g., copper) in the heat of the electric arc. While alumina can be reduced by carbon, as pointed out previously, the metal so reduced will either combine with the carbon, forming aluminum carbide; combine with carbon monoxide or dioxide, forming aluminum carbide or oxide; combine with any oxygen present; or else volatilize. In the presence of another metal, however, say copper or iron, the reduced aluminum alloys with the other metal, thereby forming an intermediate alloy. In the Cowles process, when copper is used, alloys containing 15 to 40 per cent aluminum and the remainder copper are produced, and these were diluted with copper in making aluminum bronze.

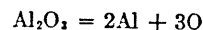
In the process, a correctly proportioned mixture of alumina, carbon, and copper is placed in an electric-arc furnace and smelted. Copper, or any other metal used for alloying, has no effect on the actual reaction, since what takes place is simple reduc-

tion of alumina by carbon at elevated temperatures, according to



During the years 1885 to 1890, the alloys made by the Cowles process could be produced at a lower price per pound of contained aluminum than substantially pure aluminum itself, and as a consequence a considerable measure of success was had. The process is obsolete, but it may have had a war revival, to produce certain intermediate or light aluminum alloys by direct reduction from alumina.

Hall Aluminum Process.—In 1886, C. M. Hall, of Oberlin, Ohio, found[5] that alumina dissolved in a liquid (fused) solution of aluminum fluoride and another metal fluoride, *e.g.*, sodium, formed an electrolyte and that the alumina could be dissociated by the electric current, according to



The electrometallurgical principle involved in the process, then, is the electrolytic decomposition of alumina dissolved in a bath of fused fluorides of aluminum and other bases; the current causes dissociation of the alumina into aluminum and oxygen without appreciably affecting the solvent. This invention caused a revolution in the aluminum industry. It should be added that C. S. Bradley applied for a patent covering the electrolytic dissociation of aluminum compounds in 1883, but this patent was not granted[14] until 1892. This Bradley patent was the cause of litigation first between the Electric Smelting and Aluminum Co. (*i.e.*, the Cowles company) and Paul Héroult regarding title to it, and second between the Cowles company and the former Pittsburgh Reduction Co. (*i.e.*, the present Aluminum Co. of America). After long litigation it was decided by the courts that the Pittsburgh Reduction Co. in using the Hall patents had infringed the Bradley patent.

In development of the Hall process, it was found that cryolite made a good solvent for alumina, and cryolite, as such, or plus calcium and aluminum fluorides, is employed for the electrolytic bath in present practice. In the process, the aluminum is liberated and sinks to the cathode, while the oxygen goes to the anode, which it attacks, burning to carbon monoxide and finally to carbon dioxide on contact with the air. The electrolysis is carried out in a carbon-lined furnace or cell, the carbon lining serving as the cathode and separate carbon electrodes as the anodes. In the Hall reduction cell, the electric current serves two important functions, *viz.*: (1) it keeps the electrolytic bath liquid by the generation of heat, and (2) it causes electrolytic dissociation of the alumina. Theoretically, the decomposition voltage required is 2.8, but in practice about three times this is actually used.

As indicated, P. L. V. Héroult, of Paris, France, brought out a process in 1886 for the preparation of aluminum by the electrolysis of alumina dissolved in cryolite, and this process is identical in principle with that of Hall. Héroult's first patent¹ called for the preparation of aluminum and aluminum alloys by the electrolysis of alumina dissolved in cryolite, and in making aluminum alloys a negative electrode of the metal to be alloyed was employed. This method was never applied commercially to the production of alloys, but it was used for aluminum. In Héroult's² second method, a process for making aluminum alloys was specified, in which alumina was melted by the electric current and electrolyzed by the same current, using a liquid metal, *e.g.*, copper, beneath the aluminum as the cathode. The resulting product is an intermediate alloy of aluminum and copper, similar to that obtained by the Cowles process. Alumina, without copper or another metal present, cannot be electrolyzed to

¹ French patent 175711, Apr. 23, 1886.

² French 170003, Apr. 15, 1887; and U. S. patent 387876, Aug. 14, 1888; and other patents.

produce aluminum, since the metal would be volatilized at the temperature prevailing. This process was operated for a short time at Neuhausen, Switzerland, but was abandoned in 1891, and the production of aluminum taken up in accordance with Héroult's first patent.

Many methods have been devised for the production of aluminum both before and since the invention of the Hall-Héroult process, but all aluminum made now is produced by this process. The older methods have been discussed at length in the books by Richards[2] and Minet[3] and need not be considered here, but it is of interest to touch briefly upon some processes that have been devised in recent years. However, none of these is now commercial.

A method for the production of aluminum directly from aluminum-bearing minerals has been patented by Tone,¹ in which aluminum ore is smelted to aluminum carbide with carbon in an electric furnace, and this is then mixed with silica and smelted to an aluminum-silicon alloy or with aluminum oxide and smelted to aluminum. The process is uneconomic, even if it is technically sound. Betts² has patented a process entailing the smelting of kaolin in a blast furnace to an iron-aluminum-silicon alloy. This alloy is then oxidized, sulphurized, or chloridized to aluminum oxide, sulphide, or chloride, and in the sulphide the compound is electrolyzed to aluminum and sulphur. In a patent by Kissock,³ an aluminum-silicate mineral is smelted with carbon to aluminum carbide, and this is converted to aluminum sulphide. The latter is electrolyzed in a suitable bath. Many carbon-smelting processes for the direct reduction of aluminum have been devised, but, as stated, these are all technically unsound. A number of patented processes call for the electrolysis of aluminum salts in aqueous solution, but these are unsound.

The fundamental principle of the Hall-Héroult process is the electrolytic dissociation of alumina dissolved in a bath of aluminum fluoride and the fluoride of one or more metals more electropositive than aluminum, *e.g.*, sodium, potassium, or calcium. The composition of the electrolytic bath is especially important, and this will be discussed briefly. Both natural and artificial cryolite are used as the base in making up baths, and the actual bath composition may vary over a fairly wide range. Cryolite melts at 995°C., and the eutectic mixture 81.5:18.5 cryolite-alumina melts at 935°C. By the addition of various salts, the melting point may be reduced to 700°C. The specific gravity of the liquid bath must be less than that of liquid aluminum at the operating temperature, since otherwise the dissociated metal would rise, instead of sink, and upset the cell. A typical bath contains 66.8 per cent aluminum fluoride and 33.2 per cent sodium fluoride. In the Hall process, the following composition has been employed for the bath: 59 per cent aluminum fluoride, 21 per cent sodium fluoride, and 20 per cent calcium fluoride. This bath dissolves 20 per cent alumina at the operating temperature. Cryolite has a specific gravity of 2.92 in the solid state and of 2.08 in the liquid state, while aluminum has a specific gravity of 2.70 in the solid state and 2.31 in the liquid state (at 900°C.). Hence at the operating temperature, the metal collects at the bottom of the bath.

The theoretical e.m.f. required for dissociation of the alumina in the process is 2.8 volts, but in practice at least three times this is necessary because of the resistance of the bath and connections and small losses here and there in the circuit. In general, irrespective of the type of furnace, each unit requires 6.5 to 7.5 volts for operation, and in starting, a wider range, 5.5 to 8.5 volts, is necessary. It is not economical to build dynamo-generators of such low voltage, and consequently 30 to 40 furnaces are connected in series; thus, the operating voltage for 35 furnaces would be 250 volts. The

¹ U. S. patent 961913, June 21, 1910.

² U. S. patent 938634, Nov. 2, 1909.

³ U. S. patent 1052727, Feb. 11, 1913.

current density varies over a rather wide range, *e.g.*, 1.5 to 3 amp. per sq. cm. in certain French furnaces, and 650 to 750 amp. per sq. ft. in some American cells. The current employed depends upon the size and the number of electrodes—8000 to 10,000-amp. lines are common, and there are larger furnaces using 15,000 to 20,000 amp. Theoretically, there should be 0.33912 g. of aluminum produced per ampere-hour, or 0.7476 lb. per 1000 amp.-hr. The theoretical anode consumption is 0.67 lb. per pound of aluminum produced, but in practice this amounts to 0.8 to 1.0 lb. The consumption of alumina per pound of aluminum produced is about 2 lb. in practice—1.888 lb. theoretically—and about 0.1 lb. of cryolite or bath material is consumed.

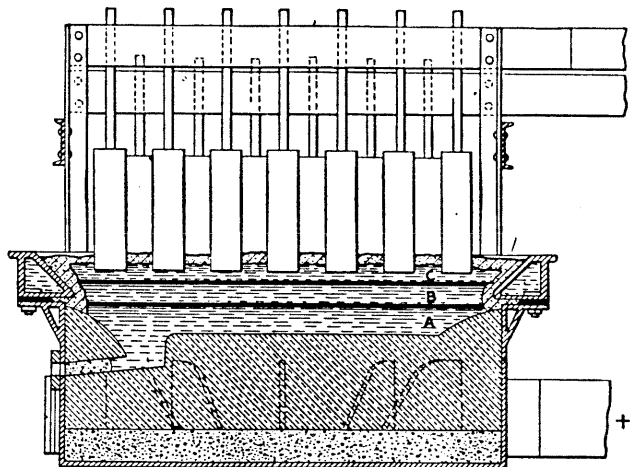


Fig. 5.—Hoopes refining cell.

About 12 kw.-hr. is required to produce 1 lb. of aluminum; hence a difference of 1 mill in the cost of power makes a difference of 1.2 cents per lb. in the cost of the aluminum.

As mentioned in a later paragraph (*cf.* Commercial Aluminum, below), the product of the Hall-Héroult reduction cell is not pure aluminum but contains appreciable amounts of impurities. Many attempts had been made to refine impure aluminum and to produce *pure* metal, but this had not been accomplished until the Hoopes process was developed. The method is described in patents[7] granted to Hoopes and others and owned by the Aluminum Co. of America. Detailed discussion of the process cannot be given here. Briefly, a cell is employed in which there are three horizontal layers; the lowest layer is a liquid aluminum-copper alloy anode, above this is a layer of fused cryolite-barium fluoride solution (the bath electrolyte), and floating on top is the cathode of pure liquid aluminum. The cell operates at about 6 volts and 20,000 amp. Cathode metal containing as high as 99.98 per cent Al has been produced in the Hoopes cell in regular operation. The mechanical, physical, and chemical properties of *pure* aluminum are markedly different from those of the ordinary 99+ per cent commercial metal, but the mechanical properties are inferior to the many carefully prepared alloys.

Aluminum-reduction Furnaces.—All furnaces now in use for the electrolytic production of aluminum, other than the Hoopes cell, are essentially the same in general design, although they vary considerably in constructional detail. The usual furnace consists of a rectangular box of mild steel lined with a refractory material of low thermal and electrical conductivity, and within this a heavier lining of rammed

carbon forming the cathode. This carbon lining is made of petroleum coke with a suitable oil or tar binder rammed in place; plates of iron may be molded in the bottom to form the cathode connection. In some furnaces, the lining is made as a separate unit, which is molded and baked similar to the anodes. There is great advantage in this type of lining, since a furnace that becomes inoperative can be renewed with a minimum of labor by simply removing the old lining and replacing it with a new unit. Figure 6 shows the general lines of the modern Hall-Héroult furnace with the anodes. In some furnaces, electrodes of carbon are embedded in the bottom of the furnace.

In all types of furnaces, the bottom is inclined toward the taphole, and each anode is arranged so that it can be operated independently of the others. Aluminum furnaces are built in various sizes, *e.g.*, 8 ft. long by 4 to 5 ft. wide by 2 ft. high, and generally rectangular shapes are now in use in place of the former round cells.

A set of anodes is suspended in the interior of each furnace, and these vary in size and length. Anodes are round, square, and rectangular in section, 3 to 16 in. in

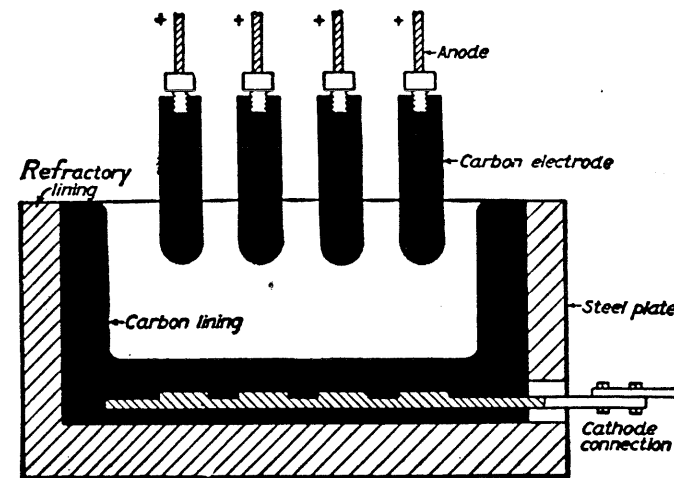


Fig. 6.—Aluminum-reduction cell.

diameter or width, and the length varies from 8 to 40 in. Anodes are suspended in the bath in groups of 8 to 12 and are closely grouped. They are clamped to a heavy frame support by suitable connections so that the group as a whole, or each individual anode, can be raised or lowered mechanically for control of the current and to ensure equal distribution. Various types of furnaces have been described by Nissen[30].

In the operation of a typical furnace, in starting, the bottom is first covered with granulated carbon shoveled in loosely, the anodes are then lowered to make contact therewith, and the current is thrown on. As the furnace heats, cryolite or a prepared bath material is added. This melts, and the anodes are raised with an increase in the bath volume, and more cryolite is added until the furnace is full. When the bath is carrying the requisite current, alumina is charged in small amounts at a time until the furnace is in full operation. Of course, other salt additions are made to the bath during the starting operation, *e.g.*, calcium fluoride and aluminum fluoride, depending upon the bath employed. Alumina is added until the bath contains 10 to 20 per cent Al_2O_3 in solution. On electrolysis, the aluminum sinks and collects on the cathode bottom, from which it is tapped periodically, and the oxygen liberated at the anode interacts therewith. In operation, the alumina content of the bath is controlled by voltmeters and incandescent lamps connected across the terminals.

When the alumina content becomes low, the furnace voltage rises from the normal 7 volts to 15 to 20 volts. The lamps are so connected that when the bath reaches a certain resistance they light, thus giving notice to the operator.

Every two or three days, according to the capacity of the furnace, the liquid aluminum is run off through a taphole in the side. This metal is remelted in order to remove occluded bath salts and is then cast into pigs, forming the primary aluminum of commerce. First-grade aluminum contains 99 to 99.5 per cent Al (by difference). The cost of production of aluminum is now 8 to 10 cents per lb.

Manufacture of Carbon Electrodes.—Since the anodes come into direct contact with the bath, they must be as free as possible from impurities, particularly iron and silica, *i.e.*, the ash content must be extremely low, and the manufacture of anodes is an important part of modern aluminum production. Petroleum coke is the best material for anode manufacture, and in practice the coke is first crushed to small nut size and

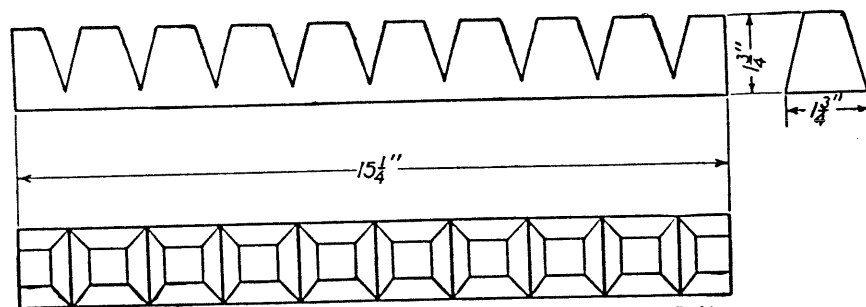


FIG. 7.—Aluminum ingot. (British Aluminum Co., Ltd.)

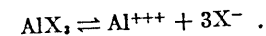
then calcined for 3 or 4 hr. at a red heat in a calcining furnace, *e.g.*, one of the Meisser type. After cooling, the calcined coke is ground, usually with waste electrodes, in a ball mill, to pass 16 to 18 mesh, of which 40 per cent passes 100 mesh. The ground coke is next mixed with a binder of pitch, or tar and oil, in steam-jacketed kneading machines, and then transferred to electrode molds or presses. The usual press is hydraulic in operation, and pressures up to 500 atm. are used.

After the electrode shapes have been formed in a press, they are air-dried and then baked in a furnace or kiln in order to remove the volatile binder. The temperature of baking is 1000 to 1400°C., depending upon the size and binder, and the heating is done slowly in order to avoid cracking. Several days are required for firing the largest sizes of electrodes. The temperature is gradually raised during the operation, and the electrodes lose about 10 per cent in weight. The furnaces are generally fired with producer gas, and the electrodes are placed in refractory saggars packed with retort-carbon powder, ground petroleum coke, or electrode scrap. Many types of furnaces are employed in baking, the common ones being the Mendheim tunnel furnace and the Meisser chamber furnace. The apparent density of petroleum-coke electrodes is 1.55 to 1.70, the real density is 1.95 to 2.05, and the ash content less than 0.3 per cent. Finished electrodes should have an electrical resistivity of about 0.0016 ohm. The production of electrodes and the apparatus used have been treated in detail by Nissen[30]. The Söderberg continuous electrode has been tried in aluminum furnaces. The Russians claim to grind a scum of carbon, alumina, and bauxite that forms in the cells with electrode material, thereby saving all of the material.

Commercial Aluminum.—The product of the reduction cell, after remelting, appears on the market as primary aluminum, and this is graded according to the amount of impurities present. The chief impurities are iron, silicon, copper, and alumina, while carbides, sulphides, sodium, nitrogen, and titanium are normally

present in very small amounts. Ordinarily, three grades of primary aluminum are marketed, *viz.*: (1) special, containing 99.5+ per cent aluminum (by difference); (2) grade No. 1 (or grade A), containing 99+ per cent aluminum; and (3) grade No. 2 (or grade B), containing 98 to 99 per cent aluminum. Primary aluminum alloys are prepared by a remelting operation in which an alloying metal is added to primary aluminum. In practice, the quality of aluminum is ordinarily based on a chemical analysis in which copper, iron, and silicon are determined, and the remainder is said to be aluminum. In 99+ per cent aluminum, the content of impurities is usually copper, trace to 0.20; iron, 0.25 to 0.60; and silicon, 0.15 to 0.40 per cent. Alumina, Al_2O_3 , is a normal impurity in commercial aluminum.

Chemical Properties of Aluminum.—The chemical properties of aluminum are remarkable and of great importance. The chemical properties of the metal and its interactions with various substances have been ably discussed by Little[6] and Mellor[10] in their books, and these may be consulted for detailed information. Aluminum is very reactive chemically and under proper conditions combines readily with oxygen, the halogens, nitrogen, sulphur, and carbon; it is readily attacked by some acids, but not at all, or slightly, by others; and it is readily soluble in alkalis. The chemical properties of light aluminum alloys are, in general, similar to those of the substantially pure metal. Aluminum is a silvery-white metal with a slightly bluish tinge, and it has great coloring power, *i.e.*, it readily whitens colored metals in alloys. Aluminum forms one series of salts in which it is trivalent, and the salts are derived from the basic oxide, Al_2O_3 . Aluminum salts are nonpoisonous; consequently aluminum cooking utensils are preferred to tinned steel utensils. On the basis of the ionic hypotheses, the salts of aluminum dissociate in aqueous solution, according to



yielding the colorless cation Al^{+++} . The ionic mobility of the cation $\frac{1}{2} Al^{+++}$ is 40.4 at 18°C., according to Heyweiller. Aluminum stands high in the electromotive series. The atomic weight of aluminum is now given as 26.97 by the International Union of Pure and Applied Chemistry.

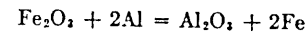
Interactions with Various Substances.—A few of the principal reactions of aluminum with various substances are indicated briefly here, and further information will be found below under Corrosion of Aluminum and Aluminum Alloys, particularly on the action of air and water. Aluminum is attacked slowly by cold acetic acid, but the rate of attack increases markedly with increasing temperature and increasing dilution of the acid. Butyric acid attacks aluminum slightly in the cold, but with boiling butyric acid the action is similar to acetic acid. Aluminum is attacked very rapidly by hydrochloric and hydrofluoric acids in all concentrations, with the evolution of hydrogen. Lactic acid has very slight effect. Cold concentrated or dilute nitric acid attacks aluminum slowly, and the metal can be employed for handling such acid. Traces of sulphuric acid in nitric acid increase the rate of attack. Oleic acid has practically no effect on aluminum. Aluminum is dissolved appreciably by hot dilute sulphuric acid, but the action of the concentrated acid is slow. Alkali hydroxides attack aluminum and its light alloys rapidly.

Aluminum interacts with carbon at high temperature to form aluminum carbide, Al_4C_3 , and carbon monoxide and dioxide interact with it, forming aluminum carbide or aluminum oxide and setting free carbon. Aluminum carbide is decomposed by water, yielding aluminum hydroxide and methane. Chlorine, bromine, and iodine all attack aluminum rapidly. Nitrogen combines directly with aluminum at moderate temperature (400 to 800°C.), forming aluminum nitride, AlN . This is attacked by water, yielding aluminum hydroxide and ammonia. Aluminum reacts with ele-

Toxic
to
some
people

mental sulphur at moderately high temperature to form the sesquisulphide, Al_2S_3 ; with phosphorus, to form a number of phosphides; and with arsenic, to form the compounds $AlAs$ and Al_3As_2 . Aluminum forms many chemical compounds, notably the alums, e.g., $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Note Oxidation of Aluminum.—The affinity of aluminum for oxygen is very great, and fine aluminum powder, or very thin foil, burns in the air, on ignition, with great violence. The thermit reduction of metallic oxides is based upon the high affinity of aluminum for oxygen. Thus, when aluminum powder is mixed with a finely divided metallic oxide and the mixture ignited, the reaction takes place with violence, yielding aluminum oxide and the metal of the metallic oxide reduced, e.g.,



The molecular heat of formation of Al_2O_3 is about 386,000 cal., or about 128,700 cal. per gram-atom of oxygen.

Metallic aluminum is normally covered with a thin film of aluminum oxide, and when heated in air, at temperatures up to the melting point, small particles of aluminum are gradually oxidized to aluminum oxide. Much experimental attention has been given to the oxidation of aluminum, but considerable uncertainty still exists as to the actual final end product of oxidation. Thus, several oxides, other than Al_2O_3 , are mentioned in the literature. Pionchon claims that the final end product of oxidation is $Al_2O_3 \cdot 3Al_2O_3$, indicating the existence of the suboxide Al_2O . Kohn-Abrest mentions AlO , and Al_2O_3 and Al_4O_7 have been described. All these seem unlikely. Rhodin, however, submits that substantially pure aluminum burns in air to form Al_2O_3 , just as iron burns to Fe_3O_4 . Aluminum quickly oxidizes if the surface is rubbed with mercury, an arborescent growth of aluminum oxide rapidly forming all over the metal. This phenomenon is known as the "activation of aluminum."

Properties of Aluminum and Aluminum Alloys.—The general physical and mechanical properties of substantially pure (commercial) aluminum have been fairly well determined, but much testing work on the properties of the light alloys is still needed. The tensile strength of aluminum is low, and the substantially pure metal finds limited and special employment for engineering construction, being valued chiefly because of its low specific gravity, great ductility, high electrical and thermal conductivity, and resistance to atmospheric corrosion. Where it is desired to take advantage of the low specific gravity of the metal, however, but where considerable strength is required, it is necessary to employ aluminum alloys.

Some excellent aluminum alloys have been developed for particular purposes, and certain of these possess tensile strength exceeding that of mild steel and the specific tenacity of alloy steels. Aluminum is malleable and ductile in the cold and can be rolled into sheet, drawn into wire, stamped and spun, and otherwise worked both hot and cold. Both the metal and its alloys are hot-short at high temperatures, and some of the alloys are cold-short.

The physical properties of aluminum and aluminum alloys are variable over a wide range depending upon the chemical composition, the physical condition, i.e., whether cast or worked, and the heat-treatment. From the commercial point of view, the following properties of aluminum and aluminum alloys are of importance in particular applications: specific gravity, hardness, tensile properties at the ordinary and elevated temperatures, modulus of elasticity, compressive strength, resistance to alternating stresses and impact, thermal expansion, growth on heating, thermal conductivity, electrical conductivity; and others. To the foundryman, the following properties of aluminum alloys are of importance from the point of view of easy casting: contraction in volume and linear contraction, fluidity and viscosity, surface tension, latent heat of fusion, melting points, and some of the other properties mentioned

above. The general physical properties of aluminum have been well summarized in Circular 76 of the National Bureau of Standards, and valuable data are to be found in

TABLE 2.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF ALUMINUM¹

Property	Units for expression	Value
Specific gravity, 20°C.....	Grams per cubic centimeter	2.70 ±
Specific gravity, liquid, 800°C.....	Grams per cubic centimeter	2.343
Solidification shrinkage.....	Per cent	6.6
Melting point.....	Degrees centigrade	658.7
Boiling point.....	Degrees centigrade	1800 ± 50
Thermal expansivity.....	Increase in length per cent of length per degree centigrade (0 to 100°C.)	0.0000239
Thermal conductivity, at 18°C.....	Gram-calories per cubic centimeter per 1 degree centigrade per second (c.g.s. units)	0.54
Latent heat of fusion.....	Gram-calories per gram	77
Latent heat of vaporization.....	Gram-calories per gram	2100
Specific heat.....	Gram-calories per degree centigrade (18 to 100°C.)	0.212
Vapor tension.....	At melting point in millimeters of mercury	1.0×10^{-43}
Specific electrical resistance.....	Microhms per cubic centimeter at 20°C.	2.82
Temperature coefficient of resistivity.....	Per degree centigrade (20 to 100°C.)	0.0039
Magnetic susceptibility.....	$H \times 10^6$, at 18°C.	+0.65
Hardness (sheet) $\frac{1}{4}H$	Brinell (10 mm., 500 kg., 30 sec.)	28
Hardness (sheet) $\frac{1}{2}H$	Scleroscope { Magnifier hammer Universal hammer	5-6 4-5
Tensile strength (sheet) H.....	Pounds per square inch	13,000
Yield point (sheet) H.....	Pounds per square inch	8500
Elongation (sheet) H.....	Per cent	15
Reduction in area (sheet) $\frac{1}{2}H$	Per cent	35
Modulus of elasticity.....	Pounds per square inch	10,000,000
Compressive strength A-132.....	Pounds per square inch	30,000
Linear contraction, 700 to 25°C.....	Per cent	1.68
Surface tension, 700°C.....	Dynes per centimeter	520
Heat of combustion to Al_2O_3	{ Calories per gram-atom of O Calories per gram-molecule	128,700 386,000
Heat of chlorination to $AlCl_3$	Calories per gram-molecule	180,000
Heat of sulphuration to Al_2S_3	Calories per gram-molecule	42,000
Electrolytic solution potential against calomel electrode.....	Volts	1.04
Atomic weight.....	O = 16	26.97

¹ Data collected from various sources.

the book by Girard[9]. The reports to the Alloys Research Committee of the Institution of Mechanical Engineers[18, 19, 24, 36] may be consulted for data on the physical properties of some aluminum alloys.

Table 2 gives a summary of the principal physical and mechanical properties of substantially pure aluminum; the figures may be compared with the corresponding properties for magnesium in the chapter on the Metallurgy of Magnesium and Magnesium Alloys in this work. Table 3 gives the average tensile properties of substan-

TABLE 3.—TENSILE PROPERTIES OF SUBSTANTIALLY PURE ALUMINUM¹

Form	Yield point, lb. per sq. in.	Tensile strength, lb. per sq. in.	Elongation on a 2-in. length, per cent	Reduction in area, per cent
Sand cast ^a	8,000- 9,000	11,000-13,000	15-25	30-40
Chill cast ^a	9,000-10,000	12,000-14,000	20-30	50-60
Sheet:				
Fully annealed.....	5,000- 6,000	12,000-15,000	15-30	30-40
Half hard.....	13,000-14,000	15,000-19,000	10-20	20-30
Hard (heavy reduction)...	20,000-24,000	22,000-26,000	2-10	5-20
Bar, hard-drawn 17S-T.....	14,000-25,000	28,000-35,000	3-10	6-20
Wire:				
17S-T.....	14,000-33,000	28,000-55,000	1-10	2-20

¹ Approximate values, from various sources.

^a But pure aluminum is rarely used for castings.

tially pure aluminum in various forms. The tensile properties of aluminum at elevated temperatures may be determined from the formula given by the Aluminum Co. of America, viz.,

$$S_t = 14,107 - 32.14t$$

where t = the temperature of testing in degrees centigrade (between 50 and 400°C.), and S_t = the tensile strength in pounds per square inch at the temperature t . The solidification shrinkage of aluminum is high, 6.6 per cent.

Physical and Mechanical Properties of Aluminum Alloys.—The general physical and mechanical properties of the light aluminum alloys vary over a wide range, depending upon the composition and the condition. The extreme limits of specific gravity of the commercial alloys are about 2.4 and 3.3, and most commercial alloys have a specific gravity under 3.0. The contraction in volume of most of the alloys is high, but less than that of aluminum, and the silicon-bearing alloys have the least contraction. Experiments by the writer [60] have shown that the linear contractions of 40 alloys vary in the range 0.95 to 1.80 per cent. The melting points of the alloys range below that of aluminum down to about 575°C., the 92:8 aluminum-copper alloy melting at 636°C. While aluminum is very soft, it can be hardened greatly by alloying, and the Brinell hardness of the commercial alloys ranges from 25 to 125 (10 mm. 500 kg., 30 sec.).

The tensile strength of the light aluminum alloys varies greatly, when cast in sand, depending upon the chemical composition, and, roughly, it lies between about 14,000 and 38,000 lb. per sq. in. Chill-cast alloys are considerably superior as to strength and ductility to sand-cast ones. In castings, the strength is a function of the size of section and the pouring temperature, being less with increase of section size and increase of pouring temperature. Gillett [22] has shown that the strength of alloys poured at high temperatures may be 10 to 20 per cent less than when poured

at low temperatures. The mechanical properties of most of the light alloys are improved by either hot- or cold-working, and the best properties of one class of alloys (duralumin) are brought out only by working followed by heat-treatment and aging. Duralumin manufactures have been made with tensile strength up to 80,000 lb. per sq. in. The elongation of sand-cast aluminum alloys varies from nil to around 12 per cent. Table 3 gives the tensile and other properties for some sand-cast aluminum alloys poured at low temperature.

Few data are available as to the compressive strength of aluminum alloys, but the range is roughly 70,000 to 100,000 lb. per sq. in. At elevated temperatures, the alloys lose strength, and most are weak above 300°C. The addition of small amounts of iron, manganese, or nickel to binary aluminum-copper alloys increases their strength at high temperatures. All the aluminum alloys are exceedingly hot-short, i.e., weak at temperatures immediately below the solidus. In fatigue (resistance to alternating stresses) the behavior of the alloys is variable, but the following alloys will withstand

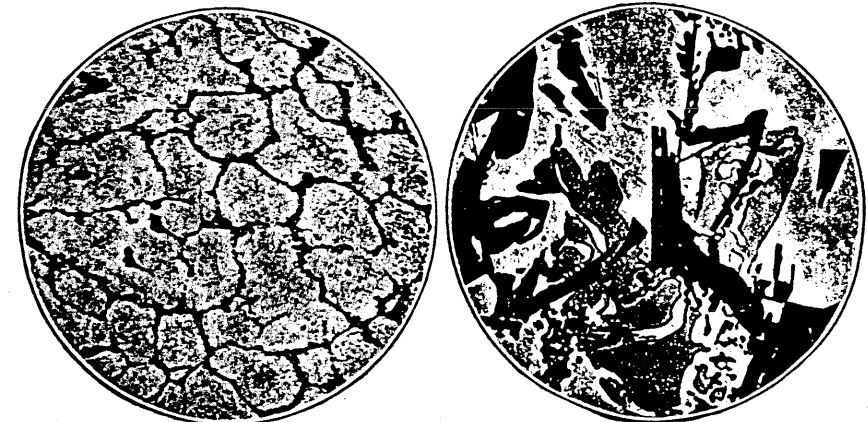


FIG. 8.—Sand-cast No. 12 alloy; etched with NaOH; $\times 75$. FIG. 9.—93:4:3 Al:Cu:Si alloy; $\times 500$ (Dix.)

10,000,000 reversals with 7000-lb. maximum fiber stress, viz., 92:8 aluminum copper; 2 to 3 per cent copper, 12 to 15 per cent zinc, and remainder aluminum; and 1.5 to 2 per cent copper, 1.5 to 2 per cent manganese, and remainder aluminum. Forged duralumin will stand 100,000,000 reversals (White-Souther) at 15,000-lb. maximum fiber stress. The Charpy impact resistance of aluminum alloys is 1 to 5 ft.-lb., notched bar, while the Izod value is 2 to 6 ft.-lb.

The coefficient of thermal expansion of the commercial light aluminum alloys varies between 22×10^{-6} and 27×10^{-6} , e.g., that of the 88:12 aluminum-copper alloy is 26.4×10^{-6} , as compared with 22.31×10^{-6} for aluminum. When a light aluminum alloy is heated, it first expands, as do most metals and alloys. After reaching about 250°C., however, the increase in size becomes quite rapid and continues for some time, even though the temperature remains constant. This is called permanent growth, since on cooling down the increase in size is not lost. All the light aluminum alloys have thermal conductivity less than that of aluminum, and, generally speaking, the greater the percentage of additive elements in an aluminum alloy, the lower the thermal conductivity. Unlike cast iron, the thermal conductivity of the aluminum alloys increases with increasing temperature; that of cast iron decreases very slightly. Whereas the thermal conductivity of aluminum = 0.504, that of the

light alloys varies in the range 0.25 to 0.48, *e.g.*, the thermal conductivity of the 88:12 aluminum-copper alloy is 0.382 at 100°C. The electrical conductivity of the aluminum alloys is lower than that of aluminum, the resistivity ranging up to 5.70 microhms per centimeter cube. The electrical resistivity of duralumin is 3.35 microhms per centimeter. A most exhaustive study of the electrical properties of numerous aluminum alloys is due to Broniewski[23].

TABLE 4.—TENSILE AND OTHER PROPERTIES OF A SERIES OF SAND-CAST LIGHT ALUMINUM ALLOYS¹

Nominal composition, elements, per cent				Elastic limit, pounds per square inch	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation on a 2-in. length, per cent	Reduction in area, per cent	Specific gravity	Brinell hardness ²	Melting point, degrees centigrade	Linear contraction, inches per foot
Al	Cu	Other metals	Mg									
100	2,000	8,000	12,000	20	35	2.70	25	658.7	0.202
96	4	10,000	16,500	5	7	2.77	45	650	0.188
92	8	8,000	12,000	19,000	1.5	2	2.85	65	636	0.172
88	12	9,000	15,000	21,000	0.5	1	2.93	70	620	0.168
95	5	16,000	22,000	1.0	2	2.62	..	630	0.175
90	10	18,000	24,000	0.5	1	2.54	..	606	0.140
98	..	2 Mn	..	4,000	7,000	17,000	7	9	2.75	40	654	0.198
95	..	5 Si ³	..	3,000	6,000	18,000	4	5	2.67	40	620	0.160
90	..	10 Si	..	5,000	10,000	20,000	2	3	2.49	50	597	0.150
87 ^b	..	13 Si ⁴	..	5,000	12,000	28,000	8	12	2.64	60	605	0.142
90	..	10 Zn	10,000	19,000	8.5	10	2.74	60	645	0.189
80	..	20 Zn	20,000	27,000	1	2	3.06	70	622	0.167
67	..	33 Zn	..	15,000	20,000	33,000	Nil	Nil	3.33	..	600	0.152
97	2	1 Mn	20,000	10	15	2.80	..	649	0.198
82	3	15 Zn	28,000	2	3	3.00	85	625	0.171
89.5	7.5	1.5 Fe ⁵	12,000	22,000	1.5	1.5	2.85	65	635	0.168
		1.5 Zn
93	4	3 Si ⁶	10,000	18,000	2.6	2.5	2.80	50
88.2	10	1.5 Fe	0.3	11,000	22,000	0.5	1	2.90	90	0.168
925.	4	1.5 Ni	2	12,000	25,000	2	1	2.80	70	0.164

¹ Data from various sources.

² 10-mm. ball, 500 kg., 30 sec.

³ Modified alloy.

⁴ Approximate Alcoa 195.

⁵ Alcoa 220.

⁶ Alcoa 43.

⁷ Approximate Alcoa 47.

⁸ Approximate Alcoa 112.

⁹ Alcoa 108.

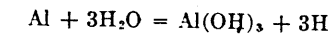
Many light aluminum alloys possess aging properties, *i.e.*, when freshly cast they may have their tensile properties enhanced by maturing at the ordinary temperature, and in the same way the machining properties may be improved. Thus, in foundry practice, it is usual to allow freshly cast parts of difficultly machineable alloys to age for some time at the ordinary temperature, when it will be found that they cut more satisfactorily than if machined soon after being taken out of the sand. In some alloys, the increase in tensile strength found on aging for one month after casting will be 25 to 30 per cent, but the elongation is decreased. The Brinell hardness increases on aging at the ordinary temperature. Heat-treatment enhances the strength and hardness of certain alloys most markedly. It is an accelerated aging.

Corrosion of Aluminum and Aluminum Alloys.—While it is often thought that aluminum and its light alloys are very susceptible to corrosion and that they, therefore, cannot be used for many purposes, these materials are actually more resistant to some corrosion influences, *e.g.*, ordinary atmospheric air, than are most simple

steels. The behavior of the metal and its alloys in different corroding media is, of course, very variable, and the resistance to corrosion of different alloys in the same media may be, and usually is, variable. Thus, the corrosion of aluminum or any aluminum alloy may be rapid in an acid-gas atmosphere, but slow in sea water or in ordinary atmospheric air; also, an aluminum-zinc alloy may deteriorate rapidly in sea water, while an aluminum-manganese alloy will corrode slowly.

The greater resistance of aluminum and its light alloys to ordinary corroding media, as contrasted with iron and steel, is explained by the surface coating of aluminum oxide which forms and protects against further corrosion. The corrosion of aluminum is affected by its purity, and for applications where specific resistance against corroding media is desired, the purer varieties will withstand attack better than less pure metal. Thus, the 99.9+ per cent metal made in the Hoopes cell is practically not corroded at all in dilute hydrochloric acid, while the ordinary 99+ per cent metal is rapidly attacked. Some of the light aluminum alloys, and also aluminum, when worked, are subject to corrosion cracking (season cracking)—a phenomenon familiar to brass metallurgists—*i.e.*, the materials exfoliate and crack in certain solutions, owing to internal stresses. Hard-worked aluminum corrodes more rapidly than annealed metal in general, and cast aluminum corrodes more rapidly than the hard-worked, because of minute pores in the former that give rise to local action. The corrosion of aluminum and its light alloys in various media has been described in many published papers, and only the more general aspects of the subject can be discussed here.

When aluminum and its light alloys are exposed to air, they become coated with a thin film consisting largely of aluminum oxide, Al₂O₃, or aluminum hydroxide, in moist air. This film, if not broken down mechanically, serves as a protective coating, and apparently it should prevent further corrosion almost indefinitely. This film, however, may be broken readily by abrasion and other mechanical influences in service, and it is also penetrable by gases and liquids, for this reason it does not serve as an effective protection unless it is fairly thick. Aluminum is attacked slowly by fairly pure atmospheric air and more rapidly by impure air. In ordinary damp air, the oxidation may be regarded rather more as a hydration of the metal taking place simultaneously with oxidation, since in the presence of moisture, the reaction



takes place and a colloidal film of aluminum hydroxide is formed. In the presence of carbon dioxide, the oxidation of the metal takes on a pitting effect, owing to the attack of carbon dioxide on the film of aluminum oxide and aluminum hydroxide, thus revealing a fresh surface of the metal to further action.

Aluminum is not attacked by distilled water, but is attacked by tap water, impure waters, and sea water, the corrosion depending upon the constitution of the waters. Oxygen is regarded as the prime cause of corrosion of aluminum by water. It has been indicated that alkalis attack the metal and its alloys rapidly, and alkaline waters are very corrosive. Alcoholic solutions and liquors have little action, and aluminum is used in the spiritous liquor and brewing industries for containers. So-called cutting solutions and compounds used for machining aluminum and its alloys have no effect unless they contain soda ash or related sodium compounds. Ether has no corrosive action. Gasoline and oils have no action. Iron salts and compounds of iron cause a blackening of the metal. Lactic acid and milk have no action, and aluminum containers are used in dairying. Aluminum is attacked by some paints.

Protection from Corrosion.—A great deal of thought has been given to the protection of aluminum and its alloys by means of various coatings. Spar varnish was the first means used, chiefly for protecting aluminum and aluminum-alloyed parts

from sea-water corrosion on seaplanes. The "browning" process of von Grotthuss was another early method in which the aluminum part was suspended in an electrolyte consisting of a sulphur compound of molybdenum with a zinc anode and electrolyzed at 60 to 65°C. The metal was soon covered with a dark brown coating which could be rolled or bent without cracking. A process at one time popular with our Air Corps was the Z-D process of Zimmerman and Daniels[66] which consisted in treating the parts to be protected with a solution of sodium silicate followed by baking.

The chief dependence now is on anodizing, which is essentially an artificial building up of the normal aluminum oxide film to a thickness that will resist corrosion. The first work on this process appears to have been done by Bengough and Stewart (British patent 223994), who made the aluminum article to be treated the anode in a chromic acid electrolyte. They also noted the ability of these oxide films to take up dyes. Certain sulphuric acid processes followed, among them being the so-called Brytal process (British patent 449162). Some further notes on anodizing will be found in the chapter on chromium.

Commercial Aluminum Alloys.—Many different alloys are now in common use. Table 5 shows a number of the standard alloys recommended by the Aluminum Co. of America, the table being based on its numbering. Because of variations produced by heat-treatment, some of the tensile strengths show a wide variation. Even the minimum values should not be used as specification limits, though ordinarily they can be depended upon. There are changes in dimensions of some aluminum alloys on aging, and most of this change can be brought about in a few hours by appropriate heat-treatment. For work requiring close tolerance, it is necessary either to allow the castings to age spontaneously or to give them a heat-treatment before machining.

It may be noted that the alloy commonly referred to as Dural is practically the Aluminum Co.'s 17S, while 24S heat-treated (24ST) is practically the European Superdural. The term "superdural" is often used to mean any low-copper heat-treatable alloy, but strictly speaking, it should refer to the alloys originally introduced by Wilm. The hardening of these alloys is due to the precipitation of a metallic compound, Mg₂Si, which occurs when the material is quenched at 480 to 500°C. and then aged. The aging may be greatly accelerated by drawing to about 100°C. The change can be delayed by keeping the material under refrigeration after quenching if subsequent forming operations are to be performed on sheets. This is now standard practice in certain plants.

Zinc duralumin is a term used to connote a class of heat-treatable alloys of the composition, for example:

	PER CENT
Copper.....	2.5
Magnesium.....	0.5
Manganese.....	0.5
Zinc.....	20.0
Aluminum (by difference).....	Remainder

Zinc duralumins may be hardened by quenching followed by aging, as in simple duralumins. These alloys have been discussed by Rosenhain and his collaborators[36]. The tensile properties of the alloys after working and heat-treatment are most remarkable. Rolled sheet, after quenching from 400°C. and re-rolling before hardening has set in, has the following properties: yield point, 64,000 lb.; tensile strength, 75,000 lb. per sq. in.; and elongation, 10 per cent. Of special duralumins, the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy has been considerably exploited, and the aluminum-magnesium silicide alloy (about 1 per cent magnesium plus sufficient silicon

to form Mg₂Si) developed as the result of investigations by Hanson and Gayler has had some use. This alloy is heat-treatable and is used for sheet, bars, rods, tubing, and special shapes. It is softer and less strong than ordinary duralumin, having a strength of about 48,000 lb. per sq. in. as rolled and heat-treated as against 62,000 lb. for duralumin.

The alloy 25S is the one most commonly used for air screws, and it appears to be about the same as the German Lautal.

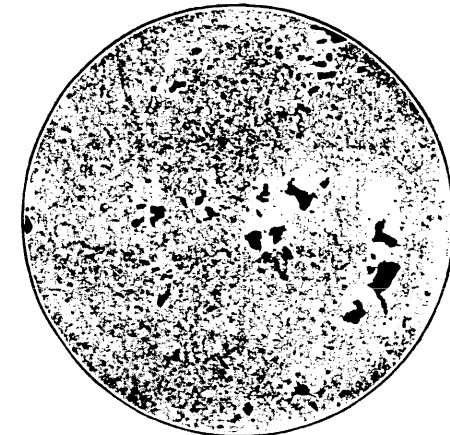


FIG. 10.—Duralumin sheet; water-quenched from 512°C. and air-aged; etched HNO₃ quench; × 200.

Casting Alloys.—Originally most aluminum castings were made in the so-called No. 12 alloy (92Al:8Cu). This alloy has been almost completely succeeded by Nos. 112 and 212 of Table 5. Number 112 is the better machining alloy, but No. 212 makes better castings. Numbers 172 and 212 are particularly recommended for thin-sectioned castings. B113 and C113 are recommended for permanent castings, as is also No. 122. This last alloy has good strength at elevated temperatures as compared with most of the aluminum alloys. Number 81 is recommended for smaller, comparatively simple die castings.

All the above are aluminum-copper alloys. The aluminum-silicon alloys are probably better casting alloys than the aluminum copper. Their fluidity and freedom from heat shortness increase to about 12 per cent of silicon, which is the Aluminum Co.'s alloy No. 13, and is apparently the aluminum silicon eutectic.

If the metal is melted under an alkaline fluoride flux, it is possible to obtain a silicon content higher than the normal eutectic composition, the castings having an extremely fine grain structure. This type of alloy is known as the "modified" alloy. The result of the treatment is largely lost on remelting.

The aluminum-silicon alloys were originally introduced by A. Pacz and are sometimes known by his name. These alloys are sometimes known in Germany as Silumin and in France as Aladar, as well as being known from their inventor as Alpax. The 12 per cent silicon alloy is reported as being used by the Germans as their chief piston alloy.

Aluminum-magnesium alloys have good mechanical properties and are particularly resistant to corrosion and tarnish. Alloys 214, B214, and 218 are recommended by the Aluminum Co. of America as considerably superior to other common sand-casting alloys of aluminum.

TABLE 5.—ALUMINUM ALLOYS IN COMMON USE
(Alloy Numbers are those of the Aluminum Co. of America. Data largely furnished by Aluminum Co. of America)

Alloy No.		Cu	Si	Mn	Mg	Zn		Fatigue limit, tons per sq. in.	Ultimate tensile strength, tons per sq. in.	Sp. gr., lb. per cu. in.
2S	W							2.5-4.3	6.5-12.0	
3S	W			1.2				3.5-5.0	8.0-14.5	
4S								3.3	9.5-12.0	0.096
11S	W ^a	5.5				Pb0.5 Bi0.5			6.0	
13	D		12.0					7.5	16.5	0.093
14S	W ^b	4.4	0.8	0.8	0.4			8.0	32.5	0.101
17S	W ^b	4.0		0.5	0.5			5.5-8.0	13.0-34.0	0.101
A17S	W ^b	2.5			0.3			6.75	21.5	
18S	W ^b	4.0			0.5	Ni2.0		7.3	27.5	0.103
24S	W ^b	4.5		0.6	1.5			6.0-9.0	13.0-36.0	
Alclad 24S									32.0-33.5	
25S	W ^a	4.5		0.8				7.5	27.5	0.101
32S	W ^b	0.9	12.5		1.0	Ni0.9		7.0	19.0	0.097
43	SC W PM D		5.0					3.2	9.5-12.0	0.097
45	SC		10.0					3.0	10.5	0.096
47	SC		12.5					3.0	13.0	0.096
51S	SC		0.9		0.6				23.5	
A51S	W		1.0		0.6	Cr0.25		5.3	16.0	0.037
52S	W				2.5	Cr0.25		8.5-9.5	14.5-20.5	
53S	W			0.7	1.3	Cr0.25		3.7-5.5	8.0-19.5	0.097
56S	W			0.1	5.2	Cr0.1				
61S	W	0.25	0.6		1.0	Cr0.25		4.0-6.2	9.0-22.5	
70S	W	1.0		0.7	0.4	10.0				
79	D	4.0	7.0							
81	D	7.0	3.0					8.0	16.0	0.103
82	D	14.0	5.0							
83	D	2.0	3.0					7.3	15.0	0.099
85	D	4.0	5.0					8.5	19.0	0.101
93	D	4.0	2.0			Ni 4.0			16.5	0.104
108	SC	4.0	3.0					4.25	10.5	0.099
A108	PM	4.5	5.5						14.0	
112	SC	7.0				1.7 Fe1.2		4.5	11.5	0.103
B113	PM	7.0	1.7			Fe1.2			14.0	
C113	PM	7.0	3.5			2.0 Fe1.2			15.0	
122	SC PM	10.0			0.2	Fe 1.2		4.7	11.5-12.5	0.103
A132	PM	0.8	12.0		1.0	Fe0.8 Ni2.5			18.0	0.097
138	PM	10.0	4.0		0.2	Fe1.0				
142	SC PM	4.0			1.5	Ni2.0		3.2-5.2	11.5-23.5	0.099
172	SC	8.0	2.5						11.5	0.102
195	SC	4.5						3.0-3.3	15.5-18.0	0.100
B195	PM	4.5	2.5							0.100
212	SC	8.0	1.2			Fe1.0		4.0	11.0	
214	SC PM				3.8			3.5	12.5	0.095

TABLE 5.—ALUMINUM ALLOYS IN COMMON USE.—(Continued)

Alloy No.		Cu	Si	Mn	Mg	Zn		Fatigue limit, tons per sq. in.	Ultimate tensile strength, tons per sq. in.	Sp. gr., lb. per cu. in.
A214	PM				3.8	1.8			13.5	0.096
B214	SC PM		1.8		3.8				10.0	
218	D				8.0			9.0	19.0	0.091
220	SC				10.0			3.5	22.5	0.092
A254	D									0.096
315	D		1.5							0.097
A334	SC	3.0	4.0		0.3			4.3	12.5	
355	SC PM	1.3	5.0		0.5			4.3	12.5-21.5	0.097
A355	SC	1.4	5.0	0.8	0.5	Ni0.8		4.3	14.0	0.099
356	SC PM	0.2	7.0	0.1	0.3	Fe0.4		4.0-4.3	14.0-20.0	0.095
406	SC			2.0				2.8	9.5	
505	D	0.5	0.5			Ni4.5				0.101
645	SC	2.5				11.0 Fe1.2		3.8	14.5	

SC—sand casting; W—wrought; PM—permanent mold casting; D—die casting.

Ultimate tensile and fatigue limits depend on the heat-treatment and condition. The figures therefore vary widely. The upper figure is usually at maximum hardness. Permanent mold castings have higher values than sand castings.

^a Will not age spontaneously; requires heat-treatment.

^b Ages spontaneously. Fabricate or refrigerate immediately after quenching.

English practice has largely developed around the use of aluminum-zinc alloys, which are represented in Table 5 by alloys 112, C113, A214, and 645. There has been prejudice in the United States against the use of the zinc alloys largely because of the labor difficulties of keeping high-zinc scrap separate from zinc-free material.

The aluminum-nickel alloy (95.5 Al:4.5 Ni) is used for die castings. The 92½ Al, 4 Cu, 1½ Mg, 2 Ni is used for sand and permanent mold castings, particularly cylinder heads; it has a good strength at elevated temperatures and good bearing characteristics (alloy No. 142). This alloy is the one often referred to as the "Y" alloy of the English National Physical Laboratories.

Melting Practice.—Aluminum and aluminum alloys are melted in various types of furnaces in practice, and there is really no standardized mode. In foundry practice, light aluminum alloys have been melted in all types of furnaces that have been used for brass and bronze, and the iron-pot furnace, so widely used for melting so-called white metals, is the only one employed for aluminum alloys that is not used for brass and bronze. While a great variety of furnaces are in commercial use, as indicated, the iron-pot furnace is generally preferred for melting aluminum alloys in foundry practice and the reverberatory-type furnace for aluminum in rolling-mill practice. The theoretical and practical aspects of aluminum and aluminum-alloy melting have been discussed at length by R. J. Anderson in published papers[37, 38, 43, 50], which may be consulted for detailed information.

One of the principal difficulties in aluminum and aluminum-alloy melting is the prevention of oxidation (dross) losses, and even with the best practice there is always considerable loss. In practice, the metal and its alloys should be heated only to the required pouring temperature or a little higher, and "soaking" of melts should be

avoided. The pouring temperature for aluminum in casting rolling ingots is preferably 700 to 750°C., while in sand practice the pouring temperature may vary between 700 and 800°C., depending upon the type of casting.

Types of Furnaces and Operation.—In foundry practice, the following types of furnaces are employed in the United States: coal-, oil-, and gas-fired reverberatory furnaces; oil- and gas-fired stationary and tilting iron-pot furnaces; coal- and coke-fired stationary and tilting crucible furnaces; oil- and gas-fired open-flame tilting, rotating, and stationary furnaces; and electric furnaces of several types. In general, ordinary brass-melting furnaces of various types have simply been adapted for

TABLE 6.—TYPICAL TENSILE PROPERTIES OF WROUGHT ALUMINUM ALLOYS AT ELEVATED TEMPERATURES
(Courtesy Aluminum Co. of America)

	Temp., °F.	Strength, lb. per sq. in.		Elongation, % in 2 in.		Temp., °F.	Strength, lb. per sq. in.		Elongation, % in 2 in.
		Yield	Tensile				Yield	Tensile	
24S-T	75	45,000	68,000	22	2-0	75	5,000	13,000	45
	300	35,000	42,000	21		300	3,500	7,500	65
	400	23,000	28,000	25		400	3,000	6,000	70
	500	10,000	14,000	40		500	2,000	3,500	85
	600	6,000	7,500	65		600	1,500	2,500	90
	700	3,500	4,500	100		700	1,000	1,500	95
A51S-T	75	40,000	47,000	20	112	75	14,000	23,000	1.5
	300	15,000	19,000	28		300	24,000	25,000	1.5
	400	5,500	7,500	58		400	15,000	19,000	1.5
	500	4,500	5,500	59		500	10,000	15,000	3.5
	600	3,500	4,500	60		600	4,500	6,500	20.0
	700	3,000	3,500	65					
52S-T	75	33,000	39,000	20	122 T-61	75	30,000	36,000	1.0
	300	22,000	25,000	17		300	30,000	35,000	1.2
	400	10,000	13,000	30		400	16,000	22,000	2.0
	500	3,500	6,000	70		500	5,000	10,000	6.0
	600	2,500	5,000	75		600	4,500	8,000	14.0
	700	2,000	2,500	90					

aluminum-alloy melting, while in aluminum rolling-mill work reverberatory and open-flame barrel-shaped furnaces have been largely employed. As indicated, the iron-pot furnace is preferred for melting aluminum alloys in founding, but open-flame furnaces are being used more widely than a few years ago.

In small foundries, and in plants where only a minor part of the output is in aluminum alloys, pit or crucible furnaces are employed largely. The electric-furnace melting of aluminum and its light alloys is receiving considerable attention, and a few installations have been made. The tendency toward the employment of furnaces of large capacity, *i.e.*, reverberatory and open-flame barrel furnaces, necessarily came through the enlargement of plant capacity.

Turning to the question of oxidation losses on melting aluminum and its light alloys—when heated in air, aluminum oxidizes to aluminum oxide, Al_2O_3 , and the

rate of oxidation increases rapidly with increasing temperatures. Hence, one of the cardinal rules in melting practice is that the melting temperature should be kept

TABLE 7.—COMPARATIVE MECHANICAL, ELECTRICAL, AND OTHER PROPERTIES OF ALUMINUM AND COPPER¹

Property	Aluminum	Copper
Specific gravity.....	2.70 ±	8.89 ±
Melting point, degrees Centigrade.....	658.7	1083
Specific heat (water = 1) at 20°C., calorie.....	0.214	0.095
Specific thermal conductivity, calories per degree Centigrade, per square centimeter per centimeter.....	0.504	0.895
Approximate relative heat conductivity (silver = 100 per cent).....	50	90
Coefficient of linear expansion, per degree Centigrade...	0.000024	0.000017
Tensile strength, hard-drawn wire (No. 10 S.w.g.) pounds per square inch.....	26,000	50,000
Tensile strength, annealed wire (No. 10 S.w.g.), pounds per square inch.....	14,000	29,000
Modulus of elasticity, pounds per square inch.....	10 × 10 ⁴	17.5 × 10 ⁴
Specific resistance in microhms per cubic centimeter at 20°C.:		
Annealed.....	2.8159	1.7241
Hard-drawn.....	2.8735	1.7585
Specific resistance in microhms per cubic inch at 20°C.:		
Annealed.....	1.1086	0.6788
Hard-drawn.....	1.1313	0.6924
Ohms per mil-foot at 20°C.:		
Annealed.....	16.939	10.371
Hard-drawn.....	17.285	10.578
Resistance of solid conductor, 1,000 yd. long by 1 sq. in. cross-section, ohms:		
Annealed.....	0.0399	0.0244
Hard-drawn.....	0.0407	0.0249
Coefficient of increase of resistance with temperature, degree Centigrade.....	0.00390	0.00393
Weight per 1,000 yd. by 1-sq. in. cross-section, pounds..	3,510	11,520
For hard-drawn conductors of equal resistance:		
Ratio of diameters.....	1.28	1.0
Ratio of sectional areas.....	1.64	1.0
Ratio of weight.....	0.5	1.0
For hard-drawn conductors of equal temperature rise:		
Ratio of diameters.....	1.18	1.0
Ratio of sectional areas.....	1.39	1.0
Ratio of weight.....	0.424	1.0

¹ According to the British Aluminium Co., Ltd.

low, and, moreover, heats should not be allowed to soak in the furnace. The oxidation product resulting on melting is known as "dross," and this ordinarily contains some

mechanically entangled metal, the percentage depending upon the care used in skimming the melts. In addition to the temperature, the constitution of the furnace atmosphere in which the metal is melted is of great importance, because of interactions that take place. Thus, in addition to reacting with oxygen, aluminum reacts with nitrogen at normal melting temperature, forming aluminum nitride, and this appears in the dross. Hence, when a furnace is operated with a great excess air supply, the dross loss is necessarily high.

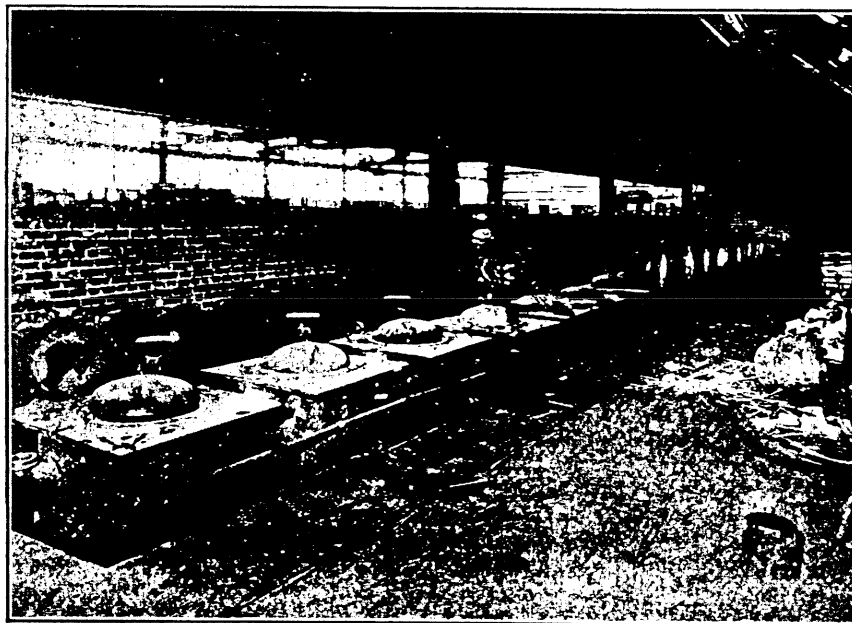


Fig. 11.—Stationary iron-pot furnaces in a foundry.

Alloying Practice.—Prior to the production of any kind of aluminum-alloy manufactures, it is first necessary to prepare the required alloys, and, in practice, the alloys may be prepared and used immediately or they may be prepared and cast into pig form for subsequent remelting. As a rule, founders prefer to make up the alloys as required rather than to purchase prepared alloys. Primary aluminum alloys of definite compositions are sold in ingot form for casting purposes, and a tremendous tonnage of secondary aluminum-alloy pig is made and sold. Primary aluminum alloys, whether pigged or used directly for casting, are made up by adding the alloying metal or metals to aluminum in a melting operation, while secondary aluminum alloys are made by running down scrap aluminum and aluminum alloys.

Foundry practice in making up alloys for casting varies considerably, and melting charges may consist of the following: (1) all-primary aluminum pig plus the necessary alloying metal, or intermediate alloy required for introducing the additive metal, plus foundry scrap or not; (2) primary aluminum-alloy pig plus foundry scrap; (3) primary aluminum, intermediate aluminum alloy, foundry scrap, and secondary metal; (4) all secondary metal plus foundry scrap. Other combinations have been employed, and these will readily suggest themselves. In making aluminum-copper alloys, it is usual to make a fixed addition of copper to the aluminum by the use of the intermediate copper-aluminum alloy of nominal composition 50:50 copper-aluminum, known in

foundry practice as "hardener." Pure copper and 33:67 and 60:40 copper-aluminum alloys are also employed. The preferred order of adding alloying elements to aluminum is copper, silicon, iron, manganese, and magnesium.

Iron may be introduced into aluminum alloys by the use of light scrap tin plate or ferroaluminum, although the avoidance of iron is usually a more important problem than its addition, while magnesium is best added in small pieces as pure magnesium, using a perforated crucible or "phosphorizer" for containing the metal. Manganese additions are usually made with 25:75 manganese-aluminum alloy, and nickel as light sheet nickel or 20:80 nickel-aluminum alloy. Silicon is added preferably by using the 50:50 silicon-aluminum alloy. Zinc, tin, and other low-melting-point metals are added as such. An intermediate alloy is essential when high-melting-point metals are to be alloyed, and the employment of these intermediate alloys is a great convenience. Most of them are brittle and can be weighed with accuracy, and their melting points are low, so that the additive metal can be introduced readily without long or high heating. Manganese may also be introduced by the use of manganese chloride in the flux. Zinc chloride in small amount is used extensively in melting and alloying practice for aluminum and its light alloys, with the object of cleaning and fluxing the melts. It is efficacious for the purpose.[59].

Secondary Aluminum and Aluminum Alloys.—Secondary aluminum is produced by remelting aluminum scraps and is used largely for remelting in foundry practice for making alloys, although some secondary metal is employed for the production of aluminum rolling ingots. Secondary aluminum alloys are made by remelting aluminum and aluminum-alloy scraps, and such alloys are used largely in foundry practice. In the remelting of aluminum-bearing scraps no refining can be done, as in the case of copper, and, consequently, secondary aluminum and aluminum alloys are normally less pure than the corresponding primary materials. The usual impurities found in secondary aluminum include copper, iron, silicon, manganese, and zinc, while secondary aluminum-alloy pig, say No. 12 alloy, may contain iron, silicon, manganese, magnesium, tin, and zinc, in addition to copper.

While all sorts of aluminum scraps are utilized in making the secondary metals and alloys—including aluminum dross and skimmings, aluminum rolling-mill scrap, aluminum fabricating scrap, particularly from utensil plants, and the corresponding aluminum-alloy scraps—the bulk of the secondary aluminum-alloy pig is produced by smelting aluminum-alloy machinings from aircraft and ordnance plants. Considerable heavy aluminum-alloy scrap results from the junking of old motor cars, and this makes good material for remelting. In machining castings, about 25 per cent of the weight is removed. In cutting and working sheet aluminum, about 20 per cent ordinarily goes into scrap. Considerable amounts of aluminum dross and aluminum-alloy dross are smelted in secondary practice. In drosses, the content of metallics may run 5 to 60 per cent, depending upon conditions, and the recovery on smelting varies from 40 to 75 per cent. The recovery on smelting borings may be 40 to 90 per cent of the metal charged, and 80 per cent is good recovery on dirty borings. Recovery naturally depends upon the quality and size of borings, *i.e.*, as to whether the chips are oily, dirty, or clean, and whether large or small.[67].

A recent proposal for scrap treatment has been put out by the Aluminum Co. of America. Aluminum aircraft scrap is to be introduced in a bath of sodium hydroxide which will dissolve the aluminum, and the solution is to be treated by the Bayer process, leaving everything else behind. G. C. Riddell has put forth the objection that zinc would also dissolve, thus contaminating the solution. The proposal was to treat it as an ordinary Bayer-process liquor.

The question of fluxes to be used in secondary aluminum work is of great importance, and a great number have been suggested, although only a few have been

extensively employed in practice. The object in using a flux is to reduce oxidation loss on melting and to cause coalescence of the metal, particularly when melting fine scraps, like borings, and drosses. In practice, the 85:15 sodium chloride-calcium fluoride flux is used most generally, but zinc chloride, several special mixtures of alkali fluorides, and cryolite are also employed. As indicated, the methods of smelting are varied, and all sorts of methods have been suggested. Heavy scrap can be readily melted with little loss, but special methods are necessary in smelting drosses, borings, and fine scraps. In running borings and drosses, the materials are often charged to a liquid heel in a crucible furnace with a flux, and the mass puddled to ensure coalescence of the melted globules, while recently the practice of puddling and working such materials in large reverberatory-type furnaces has gained ground. Drosses are normally crushed and screened to remove aluminum oxide before smelting, while borings should be run over a magnetic separator to remove included iron chips. Light scrap, like that from utensil fabrication, may be economically baled before smelting.

Aluminum Foundry Practice.—Cast-iron crucibles are very largely used in aluminum foundries. The crucible should be completely emptied each day (and sometimes oftener) and a wash given with a suspension of 7 lb. of whiting per gallon of water. Superior adhesion of the whiting to the metal can be obtained by adding 4 or 5 oz. of sodium silicate to each gallon of the mixture.

Graphite and clay crucibles are sometimes used, particularly if aluminum-silicon or aluminum-magnesium alloys are to be made, as their use minimizes any iron pickup. On the other hand, the molten metal has a tendency to pick up silicon if there is any in the crucible. Covers should be used on all crucibles in order to minimize the absorption of gas from the products of combustion.

It is impossible to judge the temperature of molten aluminum by its color as can be done with some other metals, so that some form of pyrometric control must be used.

Some good advice was contained in a paper on recommended practice for casting sponsored by the Aluminum and Magnesium Committee on Sand Castings of the American Foundrymen's Association, read at the annual meeting in St. Louis in 1944. Aluminum should be poured at the lowest temperature at which the casting will run and allow air bubbles and dross to escape from the metal. Melting temperature should also be kept low to prevent the formation of oxide and the absorption of furnace gases. Agitation of the molten metal either in the furnace or while being taken to the mold increases oxide formation and gas absorption. Continual skimming of the ladle increases the loss as oxide, since each time the protective coating is removed a new one forms. If the metal must be stirred, it should be done from the bottom upward, disturbing the surface as little as possible. Pouring time should be kept as short and with as few breaks as possible. The ladle should be kept as close to the sprue as possible, as too great a pouring height results in dross and trapped air in the final casting.

In general, temperatures in excess of 1300°F. for metal melted in direct-flame furnaces and 1500°F. for metal melted in indirect-flame furnaces are to be avoided. Metal that has been heated at too high a temperature and that has as a result absorbed too much gas does not give this out again even on prolonged standing, and metal that has become thoroughly gassed should be poured into ingots and remelted.

Molding Sand and Core Sands.—For green sand work a clay-bonded sand free from organic matter and falling within the A.F.A. classification 1G to 2G should be used. The finer sand is best for small benchwork and the coarser sand for floor work. A typical Albany sand has the following analysis: loss on ignition, 1.95; SiO₂, 80.52; Fe₂O₃, 4.83; Al₂O₃, 8.39; CaO, 0.67, MgO, 0.64; alkalis, 2.7. Sand of the above type mixed with 6 to 8 per cent water and lightly rammed gives a good surface to the castings and is open enough to permit the escape of the mold gases. Cores are made

of silica sand and sometimes molding sand held together with linseed or tung oil, while resin, dextrin, flour, or combinations of these materials are used. A table furnished by the Aluminum Co. of America gives some typical mixes. An interesting basis for the classification of foundry sands will be found in a footnote on pages 62 to 63. In general, aluminum foundry sand should fall in the classification 1G to 2G.

A notable grain refinement can be produced in aluminum by the use of small quantities of columbium and titanium. In the case of columbium $\frac{2}{100}$ to $\frac{1}{100}$ per cent produces good results. With titanium up to $\frac{1.5}{100}$ per cent can be profitably used. Too much must not be used, for if $\frac{3}{10}$ per cent of either of these elements is used the results become distinctly detrimental[75].

Apart from the solid fluxes such as the chlorides and fluorides, nitrogen gas and chlorine gas are also used in aluminum foundry practice. They are usually piped to

TABLE 8.—TYPICAL CORE SAND MIXES FOR ALUMINUM-ALLOY CASTINGS

Sands, parts by volume	Binders, parts by volume	Physical properties		General use
		Approx. A.F.A. permeability	Approx. A.F.A. compressive strength, lb. per sq. in.	
50 Bank sand 50 Washed silica sand ^a	1 Oil base 1 Dextrin base (dry bond)	50	200	Small to medium castings requiring very smooth surfaces
100 Washed silica sand ^b	1 Oil base 1½ Dextrin base (green bond)	150	550	Jacket cores and cores with thin sections
66 sharp sand 34 Bank sand	1½ Oil base	85	350	General runs of small cores
37 Bank sand	2 Pitch base	40	100	Large body and housing cores
63 Burned core sand 25 Bank sand 63 Burned core sand 12 Molding sand	3 Dextrin base (dry bond)	25	325	Side cores in contact with metal on one side only

SAND CHARACTERISTICS

Sand	Grain shape	Grain fineness
Bank sand.....	Subangular	90
Washed silica sand.....	Rounded	85
Washed silica sand.....	Rounded	65
Sharp sand.....	Angular	55
Molding sand.....	Subangular	270

^a Grain fineness, 85.^b Grain fineness, 65.

the bottom of the melting pot and allowed to bubble gently up through the metal. These gases must be free from water vapor, hydrogen, or oxygen.

If solid fluxes are used, the required amount can be determined by sprinkling a small quantity of the flux on the molten metal, stirring it into the dross, and continuing to stir in small amounts until the dross becomes powdery and granular, in which state it can be readily removed with a perforated skimmer.

Gates and Risers.—The gates and risers used in aluminum castings are much larger than those used in other nonferrous work. As laid down by the Aluminum Co. of America, castings should be gated and fed in such a way as to provide a sequence of solidification that ensures an adequate supply of molten metal to feed each section as it solidifies. The solidification should start at points furthest removed from the gating area and proceed progressively to the risers which provide liquid metal to take care of the shrinkage.

Casting Defects.—Of the various defects that may occur in sand castings of aluminum alloys, the three most frequent and important are: (1) blowholes, porosity, and general unsoundness; (2) hard inclusions; and (3) cracks. Blowholes are caused primarily by too high melting and pouring temperatures, and can be largely prevented, but general unsoundness is more difficult to overcome. As a rule, aluminum-alloy sand castings tend to be unsound, and in practice it is necessary to make tests on inspection, in certain types of castings, for porosity and related defects.

The usual method employed for detecting general or local porosity in such castings as crankcases, oil pans, manifolds, etc., is the open test with a solution of methylene blue in gasoline. In the test, this liquid is painted or smeared on the casting, and if the part is porous, the solution will seep through and show on the other side. Air-pressure, water-pressure, and steam-pressure tests are also applied, particularly to hollow castings, for detecting porosity and leaks. Porous castings may be treated, *i.e.*, the porosity closed, by several methods, of which the sodium silicate method is the one most commonly employed. In this, the castings are first soaked in concentrated (40°Bé., 1.38 sp. gr.) sodium silicate solution for an hour, then immersed for 1 to 2 min. in dilute sulphuric acid (25 per cent), and then washed in water. The casting is then dried at about 100°C. for at least 1 hr. Impregnation with tung oil is also practiced. Porous castings may also be treated with bakelite[32].

The occurrence of hard inclusions, *i.e.*, the so-called "hard spots" of foundry parlance, in aluminum-alloy castings is of interest and importance to founders and users of parts. In some cases, the percentage of machine-shop returns, owing to rejections because of hard inclusions, may be high and be the cause of considerable loss. Hard inclusions differ so widely in character that the term "hard spots" is only roughly descriptive, but hard spots are ordinarily defined as any kind of metallic or nonmetallic inclusions that cause difficulty on machining or polishing. When a machine tool strikes a hard inclusion, its edges are quickly dulled and rendered unfit for cutting. All hard inclusions may be divided into two classes, *viz.*, (1) nonmetallic inclusions and (2) metallic inclusions. Under the former are included all hard, foreign, nonmetallic particles, such as pieces of brick or cement, chunks of crucibles, core sand and molding sand, and hard clay, that may be charged with the melting stock. Metallic hard inclusions are generally traceable to iron and are due to actual iron or steel, such as nails, core wire, chaplets, or chills, charged into the furnace, or to the hard intermetallic compound FeAl₃ caused by the dissolution of iron or high iron in the melt. The subject of hard inclusions in aluminum-alloy castings has been discussed at length by the writer[45]. They can be practically entirely prevented by clean melting practice.

Cracks in aluminum-alloy castings constitute the most serious defect encountered in founding, and if the average casting loss is taken as 10 per cent, the wasters because

of cracks amount to 2 per cent of the castings poured, or 20 per cent of the total defectives. The usual commercial aluminum alloys are subject to cracking when poured into molds, owing to their large contraction in volume on freezing and their hot-shortness, and, so long as complicated castings are made, cracks must be expected in production. Some of the principal factors affecting the occurrence of cracks are the composition of the alloy; the method of molding; and the design of the castings, particularly as to thick and thin sections in contiguity. In general, the less the contraction in volume of the alloys, the less the cracking. The silicon-bearing aluminum alloys are particularly good for casting, since they have little tendency to crack—their contraction in volume is relatively low as compared with the other alloys. The causes of, and methods for the prevention of, cracks have been discussed by the writer in another place[53], where detailed information will be found.

Die Casting and Permanent-mold Casting.—Aluminum-alloy castings are made in large quantity by two other processes than sand casting, *viz.*, by die casting and permanent-mold casting, but this subject does not appear to fall within the scope of this book.

Forging.—Aluminum and its alloys crack and blister when forged at too high a temperature. The maximum temperatures at which forging should be carried on are as follows: 14S, 17S, 70S, 840°F.; 18S, 73S, 820°F.; A51S, 53S, 880°F.; 25S, 860°F.; 32S, 800°F. The upsetter heat for 14S is 800 to 900°F. The upsetter heat for 32S is 880 to 900°F.

Heat-treatment.—Both wrought and cast aluminum alloys are heat-treated commercially, and a wide field has thus been opened. Worked aluminum is annealed, as are the alloys, for the purpose of softening, and some cast alloys are annealed to release casting strains. Aluminum-alloy pistons are annealed to overcome growth and distortion. That alloys of the duralumin type are heat-treatable has been known since the investigations of Wilm in 1903, and the phenomena involved are common to many alloys. In a general way, the heat-treatability of aluminum alloys is due to the varying solubility of metallographic constituents with temperature, *e.g.*, CuAl₂ in aluminum-copper alloys and duralumin and Mg₂Si in duralumin. When such alloys are heated to moderately high temperature, *e.g.*, 500°C., more of the constituents go into solution, and, when quenched, these constituents at first remain in solution but on standing precipitate out in particles of very high dispersion. Consequently, hardening and strengthening ensue.

Worked aluminum and aluminum alloys are softened by simple anneal at 350 to 500°C., depending upon the amount of reduction and the time period of anneal. Certain cast aluminum alloys, *e.g.*, 95:5 aluminum-copper alloy, are suitable for quenching heat-treatment, and this is now being employed somewhat in practice for enhancing the properties of sand castings. The strength of the rolled and annealed 95:5 aluminum-copper alloy is increased from about 27,000 to 52,000 lb. per sq. in. by quenching and aging. When duralumin is quenched from about 500°C., it is soft and ductile, but on aging at the ordinary temperature for a few days the hardness and strength increase markedly while the elongation falls off. The aging may be accelerated by heating at 100 to 200°C. for 1 to 5 hr. The heat-treatment of duralumin has been discussed by a number of workers, including Merica and his collaborators[33a], Hanson[35], Rosenhain[56] *et al.*, Konno[42], Knerr[48], and many others. The hardening and strengthening on heat-treatment are due to the precipitation of CuAl₂ and Mg₂Si. In practice, heat-treatment is applied principally to worked duralumin, and the heating is carried out under careful pyrometric control in any suitable furnace. The quenching medium may be cold water, boiling water, or oil. Parts may be heated for quenching in a salt bath, *i.e.*, a mixture of potassium and sodium nitrates. Since quenched duralumin is soft, the material may be quenched

in water, then immediately worked to the required shape, and then allowed to age. Zinc duralumin is heat-treatable, as is the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy. Heat-treated duralumins have been used very largely in aircraft construction, though more abroad than in the United States.

Soldering and Welding.—The soldering of aluminum and aluminum alloys has attracted a great deal of interest on the part of laymen, and many patents have been taken out for solders and soldering fluxes purported to be suitable for joining aluminum and aluminum-alloy parts. Most of these are entirely useless. Aluminum parts can be soldered together fairly easily, provided the proper precautions are taken, but in all cases, irrespective of the solder employed, the joint is not permanent and fails after a short time on exposure to moisture or humid atmospheres. Joints fail because all the metals used in solders are electronegative to aluminum, and in the presence of water galvanic couples are formed, so that disintegration takes place by electrolytic corrosion. Soldering should never be done if the joint is to be exposed to moisture or if it must withstand stresses. Soldering may be regarded as satisfactory if it is desired simply "to stick parts together" and no permanence is required. While welding is the only method to be recommended for joining aluminum and aluminum-alloy parts where the joint is exposed to the weather or must be strong, still in practice it is often desired to solder, *e.g.*, in repairing slight defects in castings or in making small repairs on aluminum parts. The essential features of soldering and welding are discussed briefly below.

The limitations of soldering aluminum and its alloys have been thoroughly discussed [63], and soldering should certainly have very limited application in aluminum work, and it never should be used for the assembly of structures. Aluminum solders usually consist of low-melting-point alloys of zinc, tin, and aluminum, although many complex alloys have been suggested, containing copper, lead, iron, bismuth, antimony, and other metals in addition. The function of metals other than zinc, tin, and aluminum in a solder is not clear, and practically any other added metal is of no use, if not harmful. Most commercial aluminum solders that are useful contain 40 to 80 per cent tin, 10 to 50 per cent zinc, and 0 to 10 per cent aluminum, and the melting range is about 200 to 500°C. Their strength is 6,000 to 14,000 lb. per sq. in. and elongation 2 to 20 per cent. A ductile solder is desirable, and the presence of copper or antimony, or excess of aluminum, which causes brittleness, is to be avoided. Normally, the strength of soldered joints is not equal to the strength of the solder, and failure may occur through the solder and at the joint on breaking.

While various fluxes are recommended for soldering, these are unnecessary, and soldering may be conveniently carried out as follows: The surfaces to be soldered are carefully cleaned with a file or emery paper, and are then "tinned" or coated with a layer of the solder by heating the surface and rubbing the solder into it. The joint between the "tinned" surfaces is then made in the ordinary way with a soldering iron and the solder. In giving the preliminary coat of "tin" to the surface, the solder may be rubbed in thoroughly with a wire scratch brush. Soldering may also be carried out by first electroplating the surfaces, and the joint depends upon the firmness with which the electrodeposited metal adheres to the aluminum. Copper plating is sometimes used. Where soldering is done directly without electroplating, the effectiveness of the joint depends upon the adhesion between the aluminum and the initial layer of solder.

As indicated, the applications of soldering to aluminum and its alloys are limited. Soldering should never be used for structural assembly, but it is useful for making repairs on defective castings in the foundry [63], *e.g.*, in filling up small holes, blows, draws, etc. It should not be applied in building up large bosses or lugs, but is not dangerous for patching small defects that mar the appearance of an otherwise good

casting. The best solders are tin-zinc and tin-zinc-aluminum alloys; in the former, the composition is 15 to 50 per cent zinc and the remainder tin, and in the latter the composition is 5 to 12 per cent aluminum, 8 to 15 per cent zinc, and the remainder tin.

Autogenous welding by an oxygas method is employed extensively in the aluminum industry for making joints of substantially pure aluminum and aluminum alloys, for the assembly of structures, and for making repairs and salvaging castings. Aluminum sheet is welded in building up tanks and vessels for the chemical industry, and when sheets are joined, butt welding by the oxyacetylene or other oxygas process is suitable except in very light gage sheet where the edges are lap- or flange-welded. The oxygas process of welding the light aluminum alloys causes actual alloying of the parts to be joined and the welding material, and a fairly solid alloy can be obtained at the juncture if proper precautions are observed. In the assembly of structures, a number of methods, such as riveting, folding, sewing, doweling, and the like, have been replaced by welding. Autogenous welding consists in heating the two parts to be joined and then running liquid metal in at the juncture. In welding aluminum, it is useful to use an aluminum wire as the welding material, while for the light alloys a stick or rod of the same composition as the alloys is employed. In welding, the principal difficulty encountered is the removal of the aluminum oxide from the surfaces to be joined and in practice this is accomplished by chemical (fluxes) or mechanical (puddling) means. Electric-resistance and electric-arc welding are used for aluminum and its alloys in addition to the oxygas process. Particularly has aircraft work made use of spot welding, but this is a subject for a book in itself.

Many salts and mixtures of salts have been suggested for welding fluxes, but a flux that will dissolve aluminum oxide is required. The most suitable fluxes are mixtures of alkali fluorides and chlorides as patented by Schoop [76]. A good flux for welding consists of 0.124 lb. potassium carbonate, 0.33 lb. lithium fluoride, 2.53 lb. sodium chloride, and 3.0 lb. potassium chloride. While fluxes are generally used in welding aluminum, they are not favored in American practice for repairing castings, and in such work the aluminum oxide film is broken down mechanically by a puddling rod. Oxyhydrogen and oxyacetylene welding are done on both aluminum and its alloys, and the former is probably preferable. In welding aluminum sheet, *e.g.*, building tanks, butt welding is suitable and a feeder of aluminum wire is used. The surfaces to be joined are heated, and the wire covered with flux is melted in the torch and run into place, being puddled down and smoothed off. Welding thin stock requires considerable skill.

The repair of aluminum-alloy castings is usually done by oxyacetylene welding, using no flux, with a welding stick of the same composition as the castings. For small welds, the casting should be preheated with the torch over a considerable area in the vicinity of the spot to be welded, but for large welds and even small welds on complicated castings it is best to heat the entire casting to 300 to 450°C. in a preheater. The stock in the vicinity of the place to be welded is melted down with the torch, and the hole so made is filled with liquid alloy from the welding rod, also melted by the torch. The metal is then puddled and poked with an iron rod until a pool is formed which ensures thorough alloying with the body of the casting. The operation should be conducted rapidly, and excess alloy is scraped off while still pasty. Large castings should be cooled slowly in the furnace or in hot ashes after welding to avoid cracking. Heat-treated duralumin parts are welded in aircraft assemblies, and such welds should be heat-treated.

Several extensive bibliographies on aluminum and aluminum alloys have been published, and following are a few selected references to some of the more important publications on the subject. These will serve as a guide to the literature.

TEXTBOOKS

1. DEVILLE, H. STE-C.: "De l'aluminium, les propriétés, sa fabrication, et ses applications," Mallet-Bachelier, Paris, 1859.
2. RICHARDS, J. W.: "Aluminium: Its History, Occurrence, Properties, Metallurgy and Applications, Including Its Alloys," 3d ed., H. C. Baird & Co., Philadelphia, 1896.
3. MINET, A.: "Die Gewinnung des Aluminiums und dessen Bedeutung für Handel und Industrie," W. Knapp, Halle, 1902; translated by L. Waldo, John Wiley & Sons, Inc., New York, 1905.
4. PATTISON, J. T.: "The Manufacture of Aluminium," E. and F. M. Spon, Ltd., London, 1918.
5. U. S. patents 400664, 400665, 400667, and 400766, Apr. 2, 1889.
6. LITTLE, H. F. V.: "Aluminum and Its Congeners, Including the Rare Earth Metals" (Vol. 4 of J. N. Friend's textbook of inorganic chemistry), J. B. Lippincott Company, Philadelphia, 1919.
7. French patents 575463, 575464, 575465, 575466, and 575467, all dated 1924; British patents 223388 and 225494, Dec. 20, 1923, and 224488, Nov. 5, 1923; and U. S. patents 1534315 to 1534322, Apr. 21, 1925; and other patents.
8. MORTIMER, G.: "Aluminium," Sir Isaac Pitman & Sons, Ltd., London, 1920.
9. GIRARD, C.: "L'aluminium et ses alliages," Berger-Levrault, Paris, 1920, translated by C. M. and H. C. L. Phillips, D. Van Nostrand Company, Inc., New York, 1922.
10. MELLOR, J. W.: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. V, Longmans Green and Company, New York, 1924. (Contains a section on aluminum.)
11. ANDERSON, R. J.: "The Metallurgy of Aluminum and Aluminum Alloys," Henry Carey Baird and Co., Inc., New York, 1925, 913 pp. (A comprehensive treatise covering the subject from the mining of bauxite to the fabrication of the metal.)

PERIODICAL REFERENCES AND OTHER PUBLICATIONS

12. COWLES, E. H.: The Production of Aluminum and Its Alloys in the Electric Furnace, *J. Franklin Inst.*, Vol. 121, pp. 111-119, 1886.
13. U. S. patents 324658 and 324659, Aug. 18, 1885; and foreign patents.
14. U. S. patent 468148, Feb. 2, 1892.
15. HAYES, C. W.: Bauxite, Its Occurrence, Geology, Origin, Economic Value, *U. S. Geol. Survey, Sixteenth Annual Rept.*, pp. 547-597, Part 3, 1895.
16. GOLDSCHMIDT, H.: Aluminothermics, *Trans. Intern. Elec. Congr.*, Vol. 2, pp. 85-95, 1904.
17. RICHARDS, J. W.: "Aluminium," in "The Mineral Industry," Vol. 15, 1906, to Vol. 29, 1921, McGraw-Hill Book Company, Inc., New York. (Reviews of the aluminium industry which include data on aluminum, aluminum alloys, bauxite, etc.)
18. CARPENTER, H. C. H., and C. A. EDWARDS: On the Properties of the Alloys of Aluminium and Copper—Eighth Report to the Alloys Research Committee, *Proc. I. M. E.*, Vol. 72, pp. 57-378, 1907.
19. ROSENHAIN, W., and F. C. A. H. LANTSBERRY: On the Properties of Some Alloys of Copper, Aluminium, and Manganese—Ninth Report to the Alloys Research Committee, *Proc. I. M. E.*, Vol. 74, pp. 119-339, 1910.
20. CLACHER, W.: The Manufacture of Carbons, *Elec. Rev. (London)*, Vol. 68, pp. 99-104, 1911.

21. PHALEN, W. C.: Bauxite and Aluminum, "Mineral Resources of the U. S.," volume for 1909, part 1, pp. 561-571, *U. S. Geol. Survey*, 1911; see also succeeding volumes for years through 1915.
22. GILLETT, H. W.: Influence of Pouring Temperature on Aluminum Alloys, *Eighth Intern. Cong. Applied Chem.*, Vol. 2, pp. 105-112, 1912.
23. BRONIEWSKI, W.: Recherches sur les propriétés électriques des alliages d'aluminium, *Ann. chim. phys.*, Vol. 25, series 8, pp. 5-125, 1912.
24. ROSENHAIN, W., and S. L. ARCHBUTTS: On the Alloys of Aluminium and Zinc—Tenth Report to the Alloys Research Committee, *Proc. I. M. E.*, Vol. 76, pp. 319-441, 1912.
25. SCHIRMMEISTER, H.: Zur Kenntnis der binären Aluminiumlegierungen, *Stahl u. Eisen*, Vol. 35, pp. 649-652, 873-877, 996-1000, 1915.
26. GILLETT, H. W., and G. M. JAMES: Melting Aluminum Chips, *U. S. Bur. Mines Bull.* 108, August, 1916.
27. CARPENTER, H. C. H., and L. TAVERNER: The Effects of Heat at Various Temperatures on the Rate of Softening of Cold-rolled Aluminum Sheet, *Jour. Inst. Metals*, Vol. 18, pp. 115-169, 1917.
28. ANDERSON, R. J.: Metallography of Aluminum; Preparation and Etching of Microsections, *Chem. & Met. Eng.*, Vol. 18, pp. 172-178, 1918.
29. ANDERSON, R. J.: Annealing and Recrystallization of Cold-rolled Aluminum Sheet, *Chem. & Met. Eng.*, Vol. 18, pp. 523-527, 1918. (And a series of related papers on the same subject elsewhere.)
30. NISSEN, O.: Aluminum-manufacturing Processes Used in Europe, *Chem. & Met. Eng.*, Vol. 19, pp. 804-814, 1918.
31. HILL, J. M.: Bauxite and Aluminum, in "Mineral Resources of the U. S.," volume for 1916, part 1, pp. 159-170, *U. S. Geol. Survey*, 1919; see also succeeding volumes.
32. *Metal Ind.*, Vol. 63, p. 136, Aug. 27, 1943.
33. MERICA, P. D., R. G. WALTENBERG, and J. R. FREEMAN, JR.: Constitution and Metallography of Aluminum and Its Light Alloys with Copper and with Magnesium, *Nat. Bur. Standards Sci. Paper* 337, Aug. 16, 1919.
- 33a. MERICA, P. D., R. G. WALTENBERG, and H. SCOTT: Heat Treatment of Duralumin, *Nat. Bur. Standards Sci. Paper* 347, Nov. 15, 1919.
34. ANDERSON, R. J.: Castings of Light Aluminum Alloys, *Iron Age*, Vol. 107, 433-436, 1921.
35. HANSON, D., and M. L. V. GAYLER: The Constitution and Age-hardening of the Alloys of Aluminum with Magnesium and with Silicon, *J. Inst. Metals*, Vol. 26, pp. 321-355, 1921; and a series of related papers in the same journal in later volumes.
36. ROSENHAIN, W., S. L. ARCHBUTTS, and D. HANSON: On Some Alloys of Aluminium (Light Alloys), Eleventh Report to the Alloys Research Committee, Institute of Mechanical Engineers, August, 1921.
37. ANDERSON, R. J., and J. H. CAPPS: Gases in Aluminum Furnaces and Their Analysis, *Chem. & Met. Eng.*, Vol. 24, pp. 1019-1021, 1921; and Constitution of Gas Atmospheres in Aluminum-alloy Melting Furnaces, *ibid.*, Vol. 25, pp. 54-60, 1921.
38. ANDERSON, R. J.: Iron-pot Melting Practice for Aluminum Alloys, *Metal Ind.*, Vol. 19, pp. 189-190, 246-247, 285-287, 360-362, 1921; and *ibid.*, Vol. 20, pp. 60-61, 309-311, 1921.
39. ANDERSON, R. J.: Casting Losses in Aluminum Foundry Practice, *Trans. Am. Foundrymen's Assoc.*, Vol. 29, pp. 459-487, 1921.
40. ANDERSON, R. J.: Aluminum-copper Alloys, *Trans. Am. Electrochem. Soc.*, Vol. 40, pp. 405-434, 1921.

41. ANDERSON, R. J.: Aluminum and Bauxite, in "The Mineral Industry," Vol. 30, 1922, *et seq.*, McGraw-Hill Book Company, Inc., New York (*cf.* J. W. Richards, "The Mineral Industry," Vol. 15, 1906, to Vol. 29, 1921, reviews of the aluminum industry which include data on aluminum, aluminum alloys, bauxite, etc.).
42. KONNO, S.: An Investigation of Duralumin, *Tôhoku Imp. Univ. Science Repts.*, Vol. 11, No. 4, pp. 269-294, 1922.
43. ANDERSON, R. J.: Aluminum Melting Practice, *Foundry*, Vol. 50, pp. 737-741, 792-797, 823-826, 866-870, 919-924, 1922.
44. LADOO, R. B.: Bauxite: Occurrence, Mining, and Uses, *Eng. Mining Jour.-Press*, Vol. 114, pp. 805-809, 1922.
45. ANDERSON, R. J.: Inclusions in Aluminum-alloy Castings, *U. S. Bur. Mines Tech. Paper* 290, June, 1922.
46. ANDERSON, R. J.: Preparation of Light Aluminum-copper Casting Alloys, *U. S. Bur. Mines Tech. Paper* 287, October, 1922.
47. HOWE, G. H. and BROPHY, G. R.: Calorizing and Calite, *Gen. Elec. Rev.*, Vol. 25, pp. 267-272, 1922.
48. KNERR, H. C.: Duralumin: a Digest of Information, *Trans. Am. Soc. Steel Treating*, Vol. 3, pp. 13-42, 1922.
49. GAYLER, M. L. V.: The Constitution and Age-hardening of Alloys of Aluminum with Copper, Magnesium, and Silicon in the Solid State, *Jour. Inst. of Metals*, Vol. 28, pp. 213-244, 1922; and see other papers by Gayler and by Hanson and Gayler in Vols. 28, 29, 30. (These are important papers.)
50. ANDERSON, R. J.: Aluminum and Aluminum-alloy Melting Furnaces, *Trans. Am. Foundrymen's Assoc.*, Vol. 30, pp. 562-604, 1923.
51. CARPENTER, H. C. H., and C. C. SMITH: Tests on Work-hardened Aluminum Sheet, *Jour. Inst. Metals*, Vol. 29, pp. 29-66, 1923; and a series of related papers in the same journal by Carpenter and Elam.
52. TOUR, S.: Die Castings, *Jour. Ind. Eng. Chem.*, Vol. 15, pp. 25-28, 1923.
53. ANDERSON, R. J.: Cracks in Aluminum-alloy Castings, *Trans. A.I.M.E.*, Vol. 68, pp. 833-860, 1923.
54. DIX, JR., E. H.: Observations on the Occurrence of Iron and Silicon in Aluminum, *Trans. A.I.M.E.*, Vol. 69, pp. 957-971, 1923.
55. DANIELS, S.: Investigation of the Heat Treatment of Sand-cast Duralumin, *U. S. Air Service Information Circ.* 408, Apr. 1, 1923.
56. ROSENHAIN, W., S. L. ARCHBUTT, and S. A. E. WELLS: The Production and Heat-treatment of Chill Castings in an Aluminum Alloy ("Y"), *Jour. Inst. Metals*, Vol. 29, pp. 191-209, 1923.
57. GUILLET, L.: Un nouvel alliage d'aluminium: l'alpax, *Le Génie Civil*, Vol. 82, 413-419; 441-444, 1923; and translation by R. J. Anderson, *Trans. Am. Foundrymen's Assoc.*, Vol. 32, pp. 309-383, 1924.
58. SMALLEY, O.: The Manufacture of High-grade Aluminum and Bronze Powders, *Metal Ind. (London)*, Vol. 24, pp. 273-274; 297-298; 445-446; 493-494; 569-570; 1924 and Vol. 25, pp. 169-170; 369-371, 1924.
59. ROSENHAIN, W., and S. L. ARCHBUTT: The Use of Fluxes in the Melting of Aluminum and Its Alloys, *Trans. Faraday Soc.*, Vol. 20, pp. 179-182, 1924.
60. ANDERSON, R. J.: Linear Contraction and Shrinkage of a Series of Light Aluminum Alloys, *Trans. Am. Foundrymen's Assoc.*, Vol. 31, pp. 392-466, 1924.
61. ANDERSON, R. J., and M. E. BOYD: The Production of Aluminum-alloy Pistons in Permanent Molds, *Trans. Am. Foundrymen's Assoc.*, Vol. 32, pp. 226-286, 1924.
62. BASCH, D. and SAYRE, M. F.: Foundry Treatment and Physical Properties of Silicon-aluminum Sand Castings, *Trans. Am. Foundrymen's Assoc.*, Vol. 32, pp. 350-383, 1924.

63. ANDERSON, R. J., and M. E. BOYD: Salvage and Reclamation of Aluminum-alloy Castings by Soldering and Welding, *Trans. Am. Foundrymen's Assoc.*, Vol. 32, pp. 395-425, pp. 1924.
64. DANIELS, S., A. J. LYON, and J. B. JOHNSON: Casting and Heat Treatment of Some Aluminum-copper-magnesium Alloys, paper before the Institute of Metals Division, A.I.M.E., Milwaukee meeting, October, 1924.
65. PEDERSON, H.: "Production of Alumina from Clay," *Tids. Kjemi Bergvesen*, Vol. 3, pp. 161-164, 175-178, 1923; Vol. 4, pp. 11-17, 1924; and *Tek. Ukeblad*, Vol. 42, pp. 75-77; 83-66, 1924.
66. ZIMMERMAN, A. G.: Corrosion of Some Cast Aluminum Alloys and a Method of Protection, *Jour. Ind. Eng. Chem.*, Vol. 17, pp. 359-362, 1925.
67. ANDERSON, R. J.: Smelting Secondary Aluminum and Aluminum Alloys, *Metal Ind.*, Vol. 23, pp. 10-12, 368-370, 1925.
68. ROUSH, G. A., and M. MIYAKE: The Equilibrium of the Series Cryolite-alumina, paper before the American Electrochemical Society, Chattanooga meeting, September, 1925.
69. *Mining and Met.*, August, 1943, p. 358.
70. FLEISCHER, ARTHUR: The Kalunite Process, *A.I.M.E. Tech. Paper* 1713, February, 1944.
71. DEAN, R. S.: *Mining Met.*, August, 1943, p. 358.
72. ARCHIBALD, F. R., and C. F. JACKSON: Alumina from Clay by the Lime-Sinter Method, *A.I.M.E. Tech. Pub.* 1706, February meeting, 1944.
73. *Brick & Clay Record*, Vol. 94, p. 54, June, 1939.
74. *Mfrs. Record*, Vol. 104, p. 58, February, 1935. U.S. patents 1536681, 1536682, and 1591662.
75. WELLS, S. A. E.: *Metal Ind.*, Vol. 63, p. 136, Aug. 27, 1943.
76. U. S. Patent 922523, May 25, 1909; English patent 24283, Nov. 2, 1907; and other patents.
77. *Fortune*, December, 1943, p. 262.
78. RUNKE, S. M., and R. G. O'NEARA: Beneficiation of Arkansas Bauxite, *A.I.M.E. Tech. Pub.* 1698, February meeting, 1944.

CHAPTER II

MAGNESIUM AND BERYLLIUM

BY DONALD M. LIDDELL¹

Introduction.—Magnesium is the lightest metal of the alkali-earth division of the second group and the lightest metal employed for engineering purposes of construction. Its specific gravity is 1.74. Magnesium was little used in the United States prior to 1914, and its large-scale production began in 1915 when German imports were shut off. Its development during the present war has been one of the outstanding metallurgical developments of the period. It is probable its use was about sixty times as great in 1943 as it was in 1938, say 390,000,000 lb. as compared with 6,000,000.

Historical Survey.—In 1808, Davy first made magnesium by the reduction of magnesium oxide with potassium vapor and also by the electrolysis of anhydrous magnesium chloride, but the metal obtained was very impure. In 1830, Bussy made magnesium by reduction of anhydrous magnesium chloride with potassium, and in 1852 Bunsen prepared it by electrolysis of the anhydrous chloride in a porcelain crucible, using a carbon anode and cathode. In 1856, Matthiessen produced the metal by electrolysis of a liquid (fused) mixture of magnesium chloride and potassium chloride (4:3) plus a little ammonium chloride. The first industrial production was undertaken in France by Deville and Caron in 1863. Their process entailed reduction of a mixture of anhydrous magnesium chloride and calcium fluoride by metallic sodium, using closed iron crucibles as the containing vessels. Deville showed also at this time that magnesium could be distilled in an atmosphere of hydrogen, and he prepared very pure metal by this process.

Later, Sonstadt introduced improvements in the Deville-Caron process, whereby the metal was made by reduction of a mixture of magnesium chloride and sodium chloride with sodium in iron retorts, followed by distillation of the resulting impure metal. In 1885, von Püttner produced magnesium by a process closely resembling zinc retorting. In the process, a magnesium mineral (*e.g.*, magnesite) is first converted to the oxide, and this is reduced by carbon in heated retorts, the reduced magnesium distilling and being condensed. A number of patents were taken out after 1880 for processes specifying electrolysis of magnesium salts, both aqueous and fused, and for the reduction of magnesium compounds to metal by carbon, aluminum, etc., but these cannot be considered here. In the ordinary electrolytic process, which was developed in Germany and which supplanted Sonstadt's method, an anhydrous fused electrolyte having the composition $MgCl_2 \cdot KCl \cdot NaCl$ (or other mixture of the three chlorides) is electrolyzed in iron cells using carbon anodes, the iron of the cells forming the cathode. In this process, the magnesium is dissociated by the current, floats on top of the bath, and is ladled off. This was the principal process employed in Germany prior to the war, and the same process or a modification thereof is still employed by several producers. The first production in the United States was apparently by a company that existed in Boston from 1865–1892 and which used the Sonstadt method, but it was a small production chiefly for flashlight purposes. The first production on

¹ Consulting metallurgical engineer, New York.

a large scale in the United States was probably by Cunniff Bros. (the Rumford Metal Co.), at Rumford Falls, Me., in 1914–1915, using electrolysis of the fused chloride.

In the interval between the First and Second World Wars a process was developed for the electrolysis of magnesium oxide dissolved in a fluoride bath (strictly analogous to the Hall-Héroult process for the production of aluminum), and this period also was marked by the rise of processes depending on the reduction of magnesium oxide by carbon, by carbides, silicides, and aluminum; these new processes will be described in some detail further on.

Magnesium Sources, Ores and Minerals.—The ores, or raw materials, for the production of magnesium are extremely widely distributed, and magnesium is the fifth most abundant metal in the earth, following silicon, aluminum, iron, and calcium in the order named. Magnesium constitutes 2.24 per cent of the earth's crust (Clarke). Unlike aluminum-mineral deposits, which are found only fairly frequently in suitable composition and tonnage for the production of aluminum by electrolytic processes, magnesium deposits, notably magnesite and dolomite, occur in large amounts, widely distributed, and of suitable quality for magnesium production. Magnesium salts, notably the chloride, double chlorides, and sulphate, are found in salt beds and are constituents of saline springs, salt lakes, and the ocean.

Magnesium is never found native. Table 1 shows the chief sources of magnesium.

TABLE 1.—MAGNESIUM CONTENT OF VARIOUS SOURCES OF THE METAL

Mineral	Composition	Approximate per cent magnesium
Dolomite.....	$MgCO_3 \cdot CaCO_3$	13
Serpentine.....	$3Mg \cdot 2SiO_2 \cdot 2H_2O$	25
Olivine.....	$(Mg, Fe)_2SiO_4$	28
Magnesite.....	$MgCO_3$	28
✓ Brucite.....	$Mg(OH)_2$	41
Hydromagnesite.....	$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	26
Kieserite.....	$MgSO_4 \cdot H_2O$	14
Kainite.....	$MgSO_4 \cdot KCl \cdot 3H_2O$	9
Carnallite.....	$MgCl_2 \cdot KCl \cdot 6H_2O$	8.7
Langbeinite.....	$2MgSO_4 \cdot K_2SO_4$	11
Spinel.....	$MgAl_2O_4$	17
Talc.....	$H_2Mg_3Si_4O_{12}$	20.7–26.9
Serpentine.....	$H_4Mg_3Si_2O_{12}$	26
Sea water.....13
Brines.....	Variable

In igneous rocks, magnesium is represented by amphiboles, micas, pyroxenes, and olivine. Talc, chlorite, and serpentine are common magnesium silicates, and dolomite is frequently found in enormous mountain masses. Magnesite is mined in Australia, Austria, Hungary, Czechoslovakia, British India, Canada, Greece, Italy, Spain, South Africa, and in the Pacific coast states of California and Washington. Dolomite is mined in California, Colorado, Illinois, Ohio, Pennsylvania, and West Virginia, and various foreign countries. The sulphate ($MgSO_4 \cdot 7H_2O$) is one of the principal saline constituents of many springs. There is a peculiar deposit of pure magnesium sulphate at Basque, B. C., and this salt is obtained commercially from a dry-lake deposit near Oroville, Wash., and from the bitterns of certain California salt works. Massive magnesium fluoride is mined in Italy.

In oceanic salts, magnesium chloride makes up about 11 per cent of the total salt content, and oceanic water contains about one-eighth per cent magnesium, so that at 100 per cent recovery, it would require about 200,000 gal. of sea water to produce 1 ton of metallic magnesium. Magnesium-bearing bitterns are found at San Mateo, Calif.; Syracuse, N. Y.; Pomeroy, Ohio; Hartford, W. Va.; in the Saginaw Valley of Michigan, notably at Midland; in Colombia; in Germany; and elsewhere. The magnesium content of some inland salt lakes is high, notably Great Salt Lake, Utah, which contains 0.56 per cent magnesium. Houghton Lake, at Dana, Saskatchewan, is underlain by a 1 ft. thick layer of salts, chiefly magnesium sulphate and sodium sulphate. The principal and most famous salt-bed deposits containing magnesium minerals are the great Stassfurt salt beds in Germany (Magdeburg-Halberstadt region). The principal magnesium-bearing minerals of these beds are carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$, bischofite, $MgCl_2 \cdot 6H_2O$, and tachydrite, $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$. Magnesium-bearing salt beds also occur in Spain, Alsace, and the United States.

While minerals and ores of magnesium are abundant, in practice raw materials for production of the metal are obtained from only a few sources. These are anhydrous sodium-magnesium chloride, left after extraction of salt and bromine from brines at Midland and Ludington, Mich.; carnallite from Stassfurt; magnesite (notably from California); and magnesium carbonate, precipitated from dolomite, and some experimental production from olivine. Magnesium is made from magnesium oxide obtained from sea water in the United States, Great Britain, Italy, and Japan. Magnesium chloride is a by-product of the preparation of potassium salts in Germany and in New Mexico and can be made very cheaply. The magnesium content of magnesite as mined averages 25 per cent and that of carnallite 8 per cent.

Production of Magnesium.—Many processes for the production of magnesium have been patented, suggested, or actually used commercially. All these cannot be taken up here, but the following type processes may be mentioned: (1) reduction of magnesium compounds by a metal, *e.g.*, reduction of anhydrous fused magnesium chloride with sodium, or of magnesium oxide with aluminum; (2) reduction of magnesium oxide by carbon, followed by sublimation and condensation of the metal; (3) reduction by ferrosilicon or related compounds; (4) electrolysis of anhydrous magnesium chloride or a mixture of magnesium chloride and another chloride (sodium or potassium chloride, or both) in the fused condition; (5) electrolysis of magnesium oxide dissolved in a suitable fused bath, *e.g.*, in magnesium fluoride, in a manner similar to the Hall-Héroult aluminum process; (6) electrolysis of aqueous solutions of magnesium salts; (7) electrolysis of magnesium sulphide in a suitable fused bath.

The first process, *i.e.*, reduction of magnesium chloride by sodium, has been used commercially, but it is out of the question for commercial production now, involving as it does the use of electrolytic sodium. The second process, involving carbon reduction, forms the basis of important plants producing about 4 per cent of the United States production[7].¹ The ferrosilicon reduction process is used by the Ford Motor Co. in Michigan, Magnesium Reduction Co., Luckey, Ohio (National Lead subsidiary), the Permanente Metals Corp. in California, and the New England Lime Co. in Connecticut[40], and will be used by the Electro Metallurgical Corp. and the American Metal Co. and is apparently producing about 24 per cent of the United States production[57]. The fourth process, *i.e.*, electrolysis of fused salt mixtures high in anhydrous magnesium chloride, is largely employed at the present time, and this process is used by the Dow Chemical Co. and others to produce about 72 per cent of the United States production[57], by the Chemische Fabrik Greisheim-Elektron, and by the Magnesium Co. in England. The Mathieson Alkali Works plant at Lake Charles, La., and the Union Potash plant at Austin, Tex., will work on electrolytic methods, as

¹ References are to bibliography at the end of the chapter.

will that of the Diamond Alkali Co. at Painesville, Ohio[36]. The fifth process is analogous to the aluminum-reduction process and was developed and employed by the American Magnesium Corp., but apparently is not used at present. The sixth process is technically unsound because of the high electrolytic-solution pressure of the metal ($E_A = +1.55$ volts). The seventh process appears feasible but has not been used commercially.

The earlier methods for the production of magnesium have been described in published papers by Tucker and Jouard[2], Grosvenor[4], Phalen[10], Flusin[14], Allen[18], Boynton and his coworkers[19], Fedotieff[21], Miyake and Butts[28], Harvey[30], and others, and in many patents, *e.g.*, those of Ashcroft, Seward, Backer, and Harvey.

Magnesium Oxide from Sea Water.—The Dow Chemical Co.'s Texas plant was probably the first to use this process. The sea water is treated after sedimentation with hydrated lime made from calcined oyster shells, and the suspension is sent to Dorr thickeners, whence it goes to filters, for the production of a magnesium hydroxide cake. It would appear that a preliminary treatment with calcium hydroxide equivalent to the amount of iron and alumina in the water would be advisable if the magnesium hydroxide is to be used for the production of anhydrous magnesium chloride. It was reported to the author that Montecatini in Italy certainly gave such a preliminary treatment. In the Dow process, the magnesium hydroxide is then dissolved in hydrochloric acid for the production of magnesium chloride.

If the magnesium hydroxide is to be used for the preparation of magnesium oxide to be reduced by ferrosilicon or carbon, the use of dolomitic lime is preferable to the lime from oyster shells as the precipitant, since this gives an additional amount of magnesium hydroxide at a low cost, and the impurities introduced by the dolomite would have no adverse effect on the process (H. H. Chesny process of preparing magnesium hydroxide). For these reductions, the magnesium hydroxide is dried and calcined at 900 to 1100°C.

In the preparation of magnesium oxide from dolomite, it is important to remember that calcium oxide reacts with magnesium chloride to form magnesium oxide and calcium chloride, and that calcium is precipitated by sodium carbonate in the presence of magnesium chloride without precipitating the magnesium.

Carbon Reduction Process.—This process, usually known as the Hansgirk process, has been described by Paul D. V. Manning[44] and by T. A. Dungan[58]. It was developed in Austria several years ago by Franz Hansgirk, and a small plant was operated until an explosion destroyed the enterprise. A similar installation, on a larger scale, was made first in England by two of Dr. Hansgirk's associates and later in Korea by Dr. Hansgirk himself. In 1941, the Permanente Metals Co. at Permanente, near Los Altos, Calif., built, under the supervision of Dr. Hansgirk, a plant for the production of magnesium metal, which utilized a modification of the original process. (This plant is sometimes referred to in the literature of the metal as the Todd-California Shipbuilding plant.)

Magnesium oxide, produced as pure as possible, is mixed with carbon such as a petroleum coke. This mixture, made into briquettes with a hydrocarbon binder, is then charged continuously into an electric furnace, the magnesium oxide reacting with carbon to produce carbon monoxide and magnesium metal. The reaction is reversible, *i.e.*, the reaction tends to reverse so that carbon monoxide and magnesium produce magnesium oxide and carbon. The reaction goes in favor of producing magnesium metal at a temperature above 2000°C. Magnesium boils under atmospheric pressure at 1107°C. The equilibrium point of the reaction is reached at atmospheric pressure and stoichiometric proportions at about 1850°C. The essential point in this process is, therefore, the removal of the magnesium before it can react

with the carbon monoxide to form carbon and magnesium oxide, the process being carried on at about 2200°C.

In the original Hansgirg plant, built in Austria in 1929, this was accomplished by mixing the magnesium vapor and carbon monoxide, as it left the electric furnace, with a large quantity of refrigerated hydrogen gas. This accomplished what is termed "shock cooling" of the vapor, and the magnesium metal condensed as an impalpable powder. Some impurities were carried over with the vapor, and since the melting of a metallic powder of this fineness is extremely difficult, the next step was to form the powder into small briquettes or pellets and charge them into a retort, from which the metal was distilled under a high vacuum, to be condensed as pure crystallized magnesium.

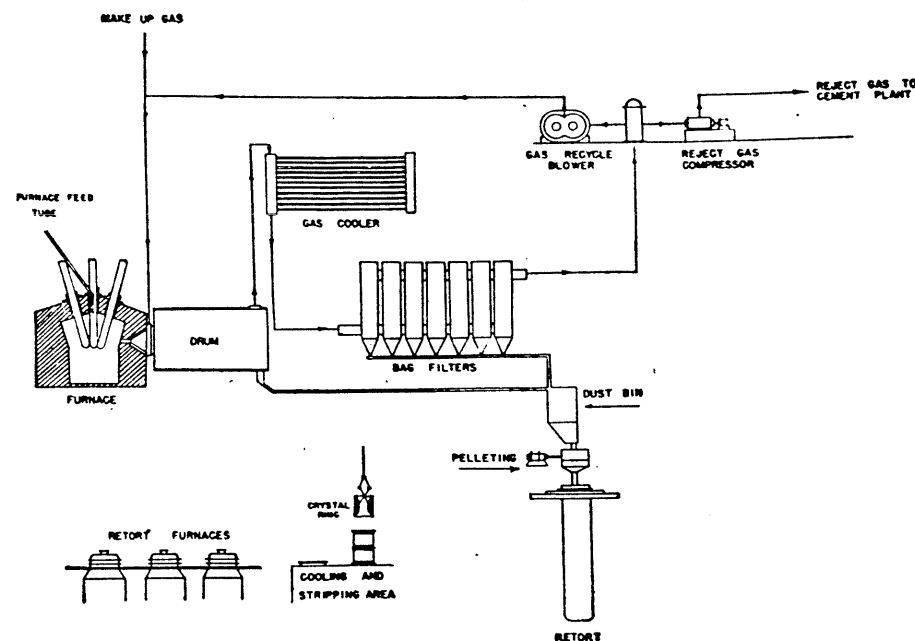


FIG. 1.—Flow sheet, Carbothermic process. (Courtesy of A.I.M.E.)

The reaction at Permanente is carried on in a graphite crucible which at its thinnest part (the junction with the roof) is 4 in. thick. The roof is composed of keyed carbon blocks 18 in. thick. The crucible is surrounded by an average thickness of about 4 ft. of fine gas carbon for insulation, and the entire assembly is inside a pressure-tight steel shell 16 ft. in diameter and 16 ft. high[58].

The electrodes are 20 in. in diameter, of machined graphite, and they enter through three holes in the roof 120 deg. apart, and each electrode is on an angle of 11 deg. with the vertical. The stuffing boxes through which these electrodes enter the crucible represent one of the greatest engineering problems in connection with the process.

The carbon monoxide and magnesium escape from the crucible through a 10 in. diameter hole about 8 in. above the coke bed where they enter the shock-chilling cone, from which the mixture of these gases with the refrigerated natural gas goes through a drum 15 ft. in diameter and 34 ft. long. About 20 per cent of the magnesium settles in this drum, and the remainder goes through bag filters. The amount of refrigerated

gas is so proportioned as to maintain a temperature of not over 250°C. in the drum. Between the drum and bag filters is a heat exchanger which cools the gas to 80°C. to protect the filters. The filter dust contains approximately 50 per cent magnesium, 20 per cent carbon, and 30 per cent MgO.

This dust is mixed with an asphalt residue in cleaning solvent or kerosene, and the paste is extruded into the sublimation retorts, where the solvent is first distilled and the asphalt coked to form a nondusting mixture.

The sublimation retorts are vertical cylindrical vessels 56 in. in diameter by 22 ft. high. The upper 8 ft. is the condenser, and there is a heat dam between the sublimation and the condensing portion of the retort. The sublimation is performed under a pressure of about 3 mm. of mercury at a temperature of about 800°C. The retort is heated by Nichrome resistance heaters, and there must be a vacuum outside the retorts as well as within to prevent the collapse of the retorts during the distillation.

Metallic magnesium resulting from the shock-cooling part of the process is extremely pyrophoric; upon exposure to air, it will instantly catch fire. Therefore, it is necessary to store the powder and handle it under an inert atmosphere such as hydrogen or methane. The handling of the vapor and of this highly inflammable magnesium powder are the sources of the principal hazards and troubles that have dogged this process since its development. Numerous fires have occurred in plants using the process, and the Austrian plant finally blew up and was completely destroyed, as before indicated. In the modification of the Hansgirg process in use at Permanente, shock cooling is not accomplished by the use of refrigerated hydrogen but by natural gas. After the removal of the magnesium dust from the resulting mixture of natural gas and carbon monoxide from the cooler, it passes into cement kilns where it is used as a fuel.

Considerable difficulty has been experienced in this process, owing primarily to the necessity of working under gastight conditions and also because of the high temperatures required in operation[44].

Important work on the carbon reduction of magnesia has also been done by H. A. Doerner. His experiments with a small-scale plant are detailed in *Chemical and Metallurgical Engineering*, August, 1942.

The cycle of cooling gas purification, if hydrogen is used, is ingenious, but unfortunately the details cannot be published.

Carbide and Allied Reduction Processes.—Apart from the direct reduction of magnesium oxide by carbon, magnesium oxide can also be reduced by calcium carbide, silicon carbide, silicon, aluminum, and various silicides, such as those of calcium, aluminum, and iron. At least experimentally, the reduction with calcium carbide and with calcium silicide have been carried on in Italy and Germany.

However, they are all of minor importance, except for the ferrosilicon reduction (Pidgeon process) and the use of finely divided aluminum of poor quality to produce first-class magnesium.

The magnesium reduction with calcium carbide is said to be most advantageously carried on as a two-stage process. The magnesium oxide is mixed with an excess of calcium carbide over that necessary to effect reduction and the mixture heated for some time at 1050 to 1150°C. The residue from this operation is mixed with additional magnesium oxide up to the theoretical quantity and there redistilled to produce additional metal.

Ferrosilicon Process.—Practice of the ferrosilicon reduction process as carried out by the Ford Motor Co. has been described by Paul D. V. Manning[44]. Dolomite is calcined to produce "dolime" and is ground to a powder with crushed 75 per cent ferrosilicon mixed with a binder. The proportion of dolomite to ferrosilicon is between five and six parts to one. The mixture is then briquetted.

Finished briquettes are charged into horizontal retorts, 10 in. in diameter and 22 ft. long, made of chrome-nickel steel, set in multiple in a furnace. After charging each retort, the condenser cover is put in place. A high-vacuum pump is started to maintain the charge in the retort under as high a vacuum as possible, and the heat is turned on around the retort. This heat causes the reaction to take place between the ferrosilicon and the calcined dolomite. Magnesium vapor is liberated and is deposited on a condenser head which extends into the end of the retort and which is cooled by water passing through its inner chamber. The magnesium metal is deposited on sleeves at the end of the retort. Approximately eight hours is required for the completion of the reaction, and about 70 lb. of magnesium per retort should result.

According to the National Research Co. of Boston, it is possible to operate large retorts on pressures as low as 0.001 to 0.025 mm. of mercury.

Contaminated aluminum scrap can be used to good advantage in this process, after powdering it, to replace the powdered ferrosilicon in part, and there seems to be no reason why the complete substitution of powdered or granulated aluminum for the ferrosilicon could not be carried out. British patents 405097 and 487836 cover the reduction of dolomite with silicon or ferrosilicon.

Retorts.—The greatest difficulty in the ferrosilicon process has been with the retorts[61, 62]. Various alloys were tried, of which the best were 35 per cent nickel,

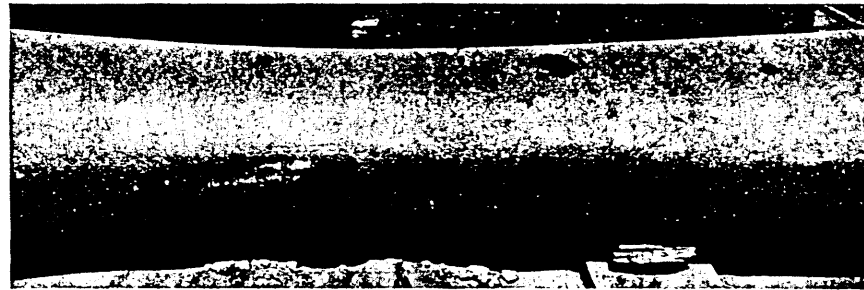


Fig. 2.—Retort after initial collapse. (Courtesy of Foley and Sebastian[62].)

15 per cent chromium; 28 per cent chromium, 20 per cent nickel; 28 per cent chromium, 15 per cent nickel; and 25 per cent chromium, 12 per cent nickel. All these seem to stand atmospheric corrosion at the operating temperature (2150°F.), but none was completely satisfactory. In general, the high-chromium alloys were superior to the high nickel.

The first retorts were 10 in. outside diameter and $\frac{7}{8}$ in. wall thickness, which was later increased to $1\frac{1}{8}$ in. wall thickness, but even then the retorts collapsed from external pressure. It was found that at the temperature of operation the retorts could be blown up to their original dimensions at an air pressure of about 90 lb. left on for a period of two or more hours. It eventually became the routine procedure to blow the retorts up every 20 days or so. A retort that survived a full year of pilot-plant service had the following composition: C, 0.33 per cent; Mn, 0.89 per cent; Si, 1.61 per cent; Cr, 26.99 per cent; Ni, 15.14 per cent; P, 0.02 per cent; S, 0.022 per cent. The actual results show that a somewhat longer average life appears to result from static casting than from centrifugal casting.

One of the problems of this process which has not yet been solved is the selection of the best and most economical type of retort. For effective reduction, the temperature must be maintained within a narrow range only slightly below the softening

point of the chromium-nickel-steel alloys used in the retorts. The rate of collapse of the tubes in the first plants was higher than expected. The wall thickness of the retorts was increased in early 1943 to $1\frac{1}{8}$ in. from $\frac{3}{4}$ in. and with this change a longer life was attained. As possible substitutes for cast-alloy retorts, two other types are being tried, one with alloy sheet wrapped and welded around a mild steel tube, the other with a layer of chromium-nickel weld metal laid on a similar steel tube. Ford is said to have changed to plain steel retorts immersed in molten glass[40].

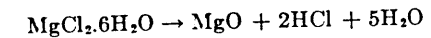
The ferrosilicon process is often called the Pidgeon process, after Dr. L. M. Pidgeon. Experimentation with 85 per cent ferrosilicon did not prove to have sufficient additional value to justify its use, and the 75 per cent grade is being used. About 1.1 lb. is used per pound of magnesium produced[35].



Fig. 3.—Full-length view after initial collapse. (Courtesy of Foley and Sebastian[62].)

Magnesium Chloride Process.—The older magnesium chloride process for the production of metallic magnesium involves three steps, *viz.*, (1) preparation of anhydrous magnesium chloride as such or in admixture with alkali chlorides; (2) electrolysis of the magnesium chloride in a cell at low voltage; and (3) purification of the resulting metal. In employing hydrous magnesium chloride as the raw material, the water must first be removed, and it should be stated at the outset that the anhydrous salt cannot be produced directly by heating the hydrous material.

When aqueous solutions of magnesium chloride are evaporated and crystallized, the salt obtained is $MgCl_2 \cdot 6H_2O$. If this salt is heated, it melts in its water of crystallization, and the reaction



takes place, so that the final product is magnesium oxide. The complete dehydration of hydrous magnesium chloride has been made the subject of many patents, and the usual methods employed entail heating the crystallized $MgCl_2 \cdot 6H_2O$ in admixture with alkali chlorides or in a current of chlorine or hydrochloric acid gas. Thus, in a process of the Dow Chemical Co., the hydrous chloride is first heated[10] at low temperature in admixture with 25 per cent sodium chloride plus a small amount of ammonium chloride, whereby about 50 per cent of the water is driven off. The partly dried mix is then cooled and reheated at higher temperature until the remaining water is removed. In the process of the Magnesium Co., the hydrous chloride is heated[80] for several hours at 150°C. in dry air; part of the water is driven off, yielding a product of the composition 73 per cent $MgCl_2$, 4 per cent MgO , and 23 per cent H_2O . This material is then reheated in a current of hydrochloric acid gas at 300°C., whereby the remaining water is removed, the magnesia converted to magnesium chloride, and a product containing 99+ per cent magnesium chloride obtained. Recovery of chlorine is made in the Dow process and of hydrochloric acid in the process of the Mag-

nesium Co. In all processes devised for the production of anhydrous magnesium chloride, the object in view is to prevent conversion of the chloride to oxide on heating. A process originally developed in Germany and later modified and used in England utilizes the electrolysis of magnesium chloride in a somewhat different way. In this process, it is necessary that the magnesium chloride be absolutely anhydrous, and it is produced by reacting calcined magnesite with carbon monoxide and chlorine to form magnesium chloride and carbon dioxide. In carrying out this process, the calcined magnesite is ground to a fine powder and mixed with lime and magnesium chloride together with fine coal and some peat moss to make the mass porous. The mixture is then briquetted or else pelletized in a rotary kiln and fed into the top of a vertical chlorination furnace. The lower part of each furnace or tower is packed with coke or other carbonaceous material so that when the mass is heated and chlorine is passed in the above reaction takes place. Magnesium chloride runs from the bottom of the furnace as a molten anhydrous liquid. This process is essentially the one that has been installed in Nevada by Basic Magnesium, Inc.[44], controlled by the Anaconda Copper Mining Co.

After preparing anhydrous magnesium chloride or a suitable mixture of this salt with alkali chlorides, the material is electrolyzed at 675 to 725°C. in a suitable cell. Although the decomposition voltage of magnesium chloride is only 3.25 volts, about 5 to 8 volts are required in practice, and the current consumption is 12 to 14 kw.-hr. per lb. of metal produced. In the process, anhydrous magnesium chloride is added to the bath from time to time as electrolysis proceeds in order to keep the bath within the required working limits of composition. Where renewal of the magnesium chloride is not made, a batch process results, and it is preferable to make the operation continuous. Various types of cells are employed. In a single-stage operation the cell is a cylindrical or rectangular iron box having carbon anodes, the iron of the cell serving as the cathode. In some cells, a cathode of steel may be suspended in the bath. The cell is heated externally in starting the process, but after electrolysis begins no further external heating is necessary, since the imposed current serves both for electrolytic dissociation of the salt and for maintaining the temperature of the bath; although it has been rumored that I. G. Farben starts with cold cells, bringing them up to working temperature entirely by the use of electric-current heating. During electrolysis the metal collects at the surface of the cathode in the form of small globules; these gradually grow larger with further deposition of metal and finally detach from the electrode, rising to the surface, where they float. The chlorine is liberated at the anode and is swept out of the cell and recovered. The magnesium is ladled out of the cell from time to time and cast into crude ingots, or is ladled directly into iron pots for purifying. The metal is fluxed in the pots with fused sodium magnesium chloride and cast into ingots or sticks. A small cell taking a 100-lb. charge yields 26 to 28 lb. of metal per 24 hr. Figure 4 shows a form of cell in which a porcelain hood is placed in the bath to keep the floating magnesium from contact with the anodically separated chlorine. In this cell, nitrogen or carbon dioxide is used to sweep out any chlorine that may penetrate to the cathode compartment. The chlorine from the anode is aspirated through the pipe shown and recovered.

The Magnesium Co., of Wolverhampton, England, employed[18] a two-stage process in order to avoid the use of a diaphragm or partitioned cell. The cell was of cast steel with a firebrick lining, fitted with a gastight cover carrying graphite anodes and means for outlet of the chlorine. The cell was charged with liquid lead for the cathode, and this was covered with the electrolyte into which the anodes dip. Means were provided for circulating both the bath and the lead cathode. The cell had a capacity of 5000 amp. at a current density of 1500 amp. per sq. ft. with a voltage drop of 5 at the terminals. The cell was self-heating and produced about 100 lb. of mag-

nesium per 24 hr. as a lead-magnesium alloy, with current efficiency of 85 per cent. The first operation was the electrolysis of the magnesium chloride electrolyte so as to produce a magnesium-lead alloy at the cathode, and in the second stage this alloy acted as the anode in another cell and the cathode consisted of a large number of steel rods immersed in the magnesium chloride electrolyte. The second cell was operated in series with the first at 5000 amp. and a voltage of 2. The total energy consumption was said to have been 8.5 kw.-hr. per lb. of magnesium produced, which seems low. The chlorine was aspirated from the cells to scrubbing towers and absorbed in milk of magnesia with the formation of magnesium chloride and chlorate, with subsequent recovery of the chlorate as $KClO_3$; the magnesium chloride was returned to the process.

Mathieson Alkali and Consolidated Mining & Smelting Co. of Canada are said to have worked out a cell that will operate even if the magnesium chloride contains 20 per cent of water[57], the effluent gas being, it is said, almost pure chlorine.

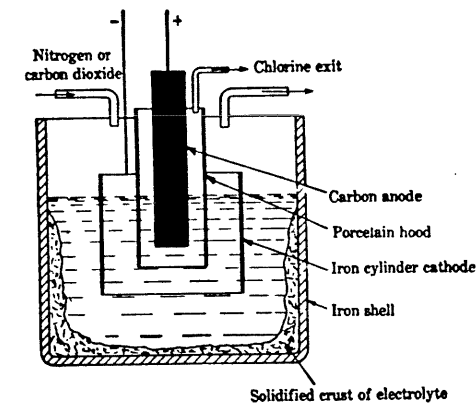


FIG. 4.—Cell for magnesium production from magnesium chloride. (Rideal.)

In a patent by Iwahashi and Kishimoto[6], an alternating current of suitable current density is passed into magnesium chloride in a cell using graphite or carbon as anode and iron as cathode; the water in the chloride is evaporated, and the salt said to be fused without decomposition; after the fused salt ceases to bubble, it is electrolyzed by direct current.

Magnesium Oxide Process.—A process for the production of magnesium that is analogous to the Hall-Héroult process for the reduction of aluminum was patented by Seward[7] and by Harvey[8] and was used by the American Magnesium Corp. In this process, substantially pure magnesia, MgO , was dissolved in a liquid (fused) electrolyte, consisting of about equal parts of magnesium fluoride and barium fluoride plus sufficient sodium fluoride to give the required fluidity, and electrolyzed. The magnesia was prepared by the calcination of magnesite obtained from the Pacific coast and shipped to the works at Niagara Falls, N. Y. (In an older patent by Seward and von Kügelgen[9], a process was disclosed for the production of aluminum magnesium alloys by electrolyzing magnesium oxide dissolved in magnesium fluoride plus lithium fluoride, using liquid aluminum as the cathode.) The magnesium-oxide process is discussed by Harvey[30].

The cell or furnace used in the magnesium oxide process may be conveniently described by reference to Figs. 5 and 6. The former shows a transverse section of the furnace, and the latter is a plan. In the figures, 1 is a wrought-iron vessel supported

on blocks 2, and 3 represents the solidified portion of the bath 4. The cathodes are represented by 5, which consist of iron or steel castings extending longitudinally through the furnace and projecting through apertures 6 in the bottom. A layer of asbestos 20 is placed between the cathodes and the furnace shell. The anodes are shown at 9, and these are of graphite or carbon, suspended in the bath. A layer of

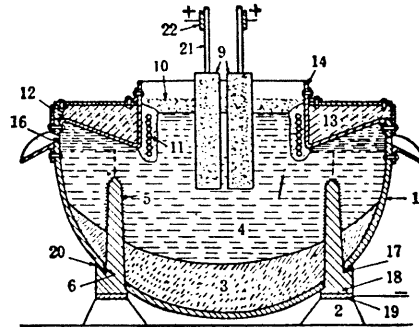


Fig. 5.—Magnesium reduction furnace. (Seward.)

magnesium oxide 10 is maintained on top of the bath as a source of raw material. Cooling pipes 11 are arranged between the cathodes and anodes so as to cause solidification of a portion of the bath to form vertical partitions of insulating material. Hoods or collecting chambers are shown at 12 receiving the liquid magnesium which ascends from the cathodes; these chambers are made of cast or sheet-metal casings 13 placed near the surface of the bath and suitably cooled. They are shown as supported

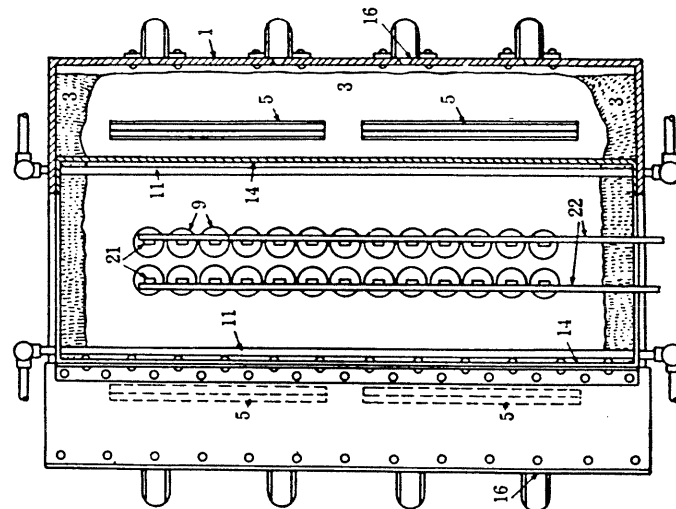
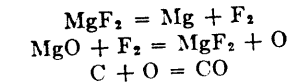


Fig. 6.—Plan of magnesium reduction furnace. (Seward.)

from the upper edges of the side walls of the furnace shell 1. The inner wall 14 of each hood is situated sufficiently close to the cooling pipes 11 so that the mass of solidified salts extends to the wall 14 and seals the space between the wall and the pipes. The liquid metal collected in the hoods or chambers may be drawn off continuously or tapped intermittently from tapholes 16. The cathodes 5 are formed with shoulders

17 for receiving the weight of the furnace, and have flat bottoms 18 which rest on flat copper bus bars 19. The anodes are carried by rods 21 and fastened to bus bars 22. In operation of the process, the bath is maintained at about 950°C. and its specific gravity at about 3.2. The magnesium oxide is added to the bath around the anodes at frequent intervals. The current may be 9000 to 13,000 amp. at an e.m.f. of 9 to 16 volts. The average current efficiency may be taken as 50 per cent with a power efficiency of 40 per cent. The dissociated oxygen burns at the carbon anodes; the magnesium is liberated at the cathodes and rises into the collecting chambers from which it is removed. The metal was refined by remelting with a flux, and specially pure metal was prepared by volatilizing the crude magnesium and condensing it.¹

Magnesium oxide is only slightly soluble in the fluoride bath—in which respect it differs considerably from aluminum oxide—the solubility being only about 0.1 per cent. Strictly speaking, therefore, the process is probably not a direct electrolysis of the oxide. It has been suggested that the mechanism is as follows:



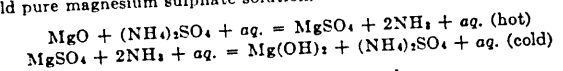
Commercial Forms of Magnesium.—Substantially pure magnesium is supplied to the trade in the form of sticks, ingots, blocks, rods, bars, tubes, sheets, plate, extrusions, wire, powder, foil, and ribbon. Powder is made 40 to 200 mesh, depending upon requirements. For deoxidizing, the metal is furnished as sticks or in the form of extruded ingot with diameter of about 1¼ in. Flashlight powder usually runs 100 to 150 mesh, while powder for signal lights in marine and military work is usually 50 mesh. Sheet and plate are available in almost any thickness, while rod is produced from ⅜ to 1¼ in. Tubing is made up to 1¼ in. outside diameter, and wire is furnished from No. 36 to No. 00 B. & S. gauge. Ribbon is usually made ⅜ in. wide by 0.006 in. thick. Sand and permanent-mold castings are made in both magnesium and its light alloys.

The Nicol process for the production of magnesium powder is to atomize the molten metal by a high-velocity stream of nitrogen. Table 4, page 60, gives a number of the commonest alloys, as well as the specifications for Grades A, B, and C.

Chemical Properties of Magnesium.—The impurities in magnesium may be divided into two classes, *viz.*, metallic and nonmetallic. The former include aluminum, barium, calcium, copper, iron, silicon, sodium, and potassium. The nonmetallic impurities are usually salts of magnesium such as the oxide and chloride, and chlorides of calcium, potassium, and sodium, as well as occluded bath material and carbon. The bulk of the nonmetallic impurities may be eliminated by a remelting operation.

Pure magnesium (99.99+ per cent) is a silvery-white metal. It consists of three isotopes of masses 24, 25, and 26, in the relative amounts of 7:1:1, yielding a mean atomic weight of 24.336, as compared with the chemical value of 24.32. Magnesium is a basic element and forms salts with mineral and many organic acids. The metal does not oxidize in dry air, but when exposed to moist air it loses its silvery luster and becomes coated with a film of the oxide and possibly carbonate (and hydroxide).

¹ One of the problems of this process is to produce a pure magnesium oxide, since the electrolyte will be contaminated by the progressive building up of any impurities in the added MgO. C. E. Dolbear claims a cyclic process for the production of the pure oxide, based on (1) boiling impure magnesium oxide with ammonium sulphate, the magnesia going into solution; (2) passing the liberated ammonia into cold pure magnesium sulphate solution.



The reaction is said to be applicable to magnesium carbonate also.

Magnesium reduces most oxides, liberating the corresponding metal or nonmetal. Magnesium has a high heat of combustion, the heat of formation of magnesium oxide, MgO , being about 146,000 cal. per gram-atom. The molecular heat of formation of Al_2O_3 is about 386,000 cal., or about 128,700 cal. per gram-atom. The explosibility of magnesium dusts is high, being about 114 as compared with 100 for standard Pittsburgh coal dust. The metal (particularly in powder or ribbon form) burns easily in air and with an intense white light, very rich in actinic rays. This property makes magnesium valuable in photographic work for flashlights. The spectrum of burning magnesium more nearly resembles that of the sun than any other element. Magnesium does not burn directly in the air to oxide, but is converted first to the nitride, which then burns to the oxide. The reaction is accompanied by a faint yellow glow, followed by the peculiar incandescence and white light. Massive magnesium does not readily burn in air except at temperatures far above the melting point.

Dilute acids dissolve the metal rapidly, with violent evolution of hydrogen. Caustic alkali solutions have no action, but hot aqueous solutions of ammonium salts attack it. Strong sulphuric acid acts slowly on magnesium, and mixed acid (sulphuric plus nitric) has slow action at the ordinary temperature. At 20°C. water does not attack the metal, but at 100°C. water is slowly decomposed with the formation of magnesium oxide and hydrogen. The action on hot water is thought to be due to galvanic action between the metal and the impurity iron therein. Magnesium unites with nitrogen below the melting point to form magnesium nitride, Mg_3N_2 , and phosphorus reacts with it to form the phosphide (Mg_3P_2). With boron it forms the boride (Mg_3B_2), and it reacts with carbon to form the carbides (MgC_2 and Mg_2C_3). The metal reacts with hydrocarbon gases to form these carbides, setting free hydrogen. It does not react with hydrogen but can be distilled in an atmosphere of this gas. In general, magnesium resists the attack of alkalis and hydrofluoric acid, but is attacked by saline solutions and most acids[30]. One use of potential importance after the war is the possibility of using the metal on a large scale to synthesize organomagnesium halides, such reagents being known as "Grignard's reagents."

Corrosion.—The information given above as to the action of chemical reagents on magnesium is suggestive in determining the corrodibility of the metal and its alloys. Magnesium and its alloys are more corrodible than aluminum and aluminum alloys when exposed to the ordinary corrosive agents. But substantially pure magnesium and light alloys made from such metal exhibit adequate corrosion resistance to ordinary air; they are attacked by solutions of acid salts, neutral solutions of acid salts, and especially by halogen salts. Gasoline, kerosene, and lubricating oils have no action. Solutions of cellulose esters dissolve the metal. Both the metal and its alloys can be protected from ordinary atmospheric and other mild corrosives by painting with lacquers, varnishes, and paints, and by special coatings. Thus, treatment in a bath of sodium bichromate, copper nitrate, and nitric acid causes formation of a colored oxidized layer, probably some copper compound, that protects against atmospheric corrosion. Backer[11] has patented a coating process in which a strongly adherent coating of magnesium hydroxide, $Mg(OH)_2$, is put on by heating the metal or its alloys in water or steam to temperatures above 100°C. for 15 min. under ordinary or raised pressures. The corrosion of magnesium by water can be inhibited by the presence of a small percentage of potassium dichromate in the water. W. S. Loose has patented the use of solutions of hydrofluoric acid, hydrofluosilicic acid, boric acid, and acid and neutral fluorides, followed by treatment with an arsenic compound (assigned to Dow Chemical Co.)(45).

Physical and Mechanical Properties of Magnesium.—Magnesium is the lightest metal used for structural purposes, having a specific gravity of 1.74. The metal weighs 109 lb. per cu. ft. The specific gravity in the liquid state (at 673°C.) is 1.56,

and the solidification shrinkage is 4.2 per cent. The low value 1.74 for the specific gravity makes an equal volume of magnesium weigh about two-thirds as much as aluminum. Magnesium is slightly malleable when cold but very malleable and ductile at 350 to 450°C. The metal and certain alloys can be cast readily in iron molds and dry-sand molds and also worked into shapes. Both magnesium and its light alloys machine easily and take a fine finish. When heated *in vacuo*, magnesium sublimes and deposits in crystals. Table 2 gives a summary of the physical and mechanical properties of magnesium; the figures may be compared with the corresponding properties for aluminum in the chapter on the Metallurgy of Aluminum and Aluminum

TABLE 2.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF MAGNESIUM¹

Property	Units for expression	Value
Specific gravity, 20°C.....	Grams per cubic centimeter	1.7388
Specific gravity, liquid, 673°C.....	Grams per cubic centimeter	1.562
Melting point.....	Degrees Centigrade	651
Boiling point.....	Degrees Centigrade	1120
Thermal expansivity.....	Increase in length per unit of length per degree Centigrade (0 to 100°C.)	0.0000259
Thermal conductivity.....	Gram-calories per centimeter cube per degree centigrade per second (c. g. s. units).	0.350
Latent heat of fusion.....	Gram-calories per gram	70
Latent heat of vaporization.....	Gram-calories per gram	1,700
Specific heat.....	Gram-calories per degree Centigrade (20 to 100°C.)	0.249
Specific electrical resistance.....	Microhms per centimeter cubed, at 20°C.	4.46
Temperature coefficient of resistivity	Per degree Centigrade (20°C.)	0.0040
Magnetic susceptibility.....	$H \times 10^6$, at 18°C.	+0.55
Hardness (cast).....	Brinell (10 mm., 500 kg., 30 sec.)	30
Hardness (cast).....	Scleroscope:	
	Magnifier hammer	20
	Universal hammer	12
Tensile strength (cast).....	Pounds per square inch	13,000
Yield point (cast).....	Pounds per square inch	3,000
Elongation (cast).....	Per cent	6
Reduction in area (cast).....	Per cent	6
Compressive strength (cast).....	Pounds per square inch	32,000
Transverse strength (cast).....	Pounds per square inch	32,000
Heat of combustion to MgO	Calories per gram-atom	146,000
Heat of chlorination to $MgCl_2$	Calories per gram-molecule	152,000
Heat of sulphuration to MgS	Calories per gram-atom	80,000
Electrolytic solution potential against calomel electrode.....	Volts	2.82
Atomic weight.....	$O = 16$	24.32

¹ Data collected from various sources.

Alloys in this work. Magnesium is a good bearing metal. The mechanical properties of some magnesium alloys are discussed below under Alloys. Magnesium has low proportional limit and ductility, which features preclude its use for some purposes. Moore[29] gives some tests on the mechanical properties of the metal and one alloy.

Magnesium Alloys.—Magnesium-rich alloys are the lightest known useful alloys for engineering construction, their specific gravity falling in the range 1.75 to 1.90, roughly. Their tensile strength lies in the range 20,000 to 50,000 lb. per sq. in., depending upon the alloy and the condition, *i.e.*, whether cast or worked. Magnesium forms alloys with most metals, and the commercial alloys are represented by certain magnesium-zinc, magnesium-aluminum, magnesium-cadmium, magnesium-aluminum-zinc, magnesium-aluminum-cadmium-copper, magnesium-aluminum-zinc-manganese, and other alloys. Magnesium-zinc alloys are represented by the so-called "Elektron metal" of the Chemische Fabrik Griesheim-Elektron, while magnesium-aluminum alloys are made by the Dow Chemical Co. under the name Dowmetal. Substantially pure magnesium and an alloy of the nominal composition 99.5:0.5 magnesium-zinc have been marketed under the name "cork metal."

Some tests have been reported by Beckinsale[15] on the properties of German Elektron metal of the nominal composition 94.5:5:0.5 magnesium-zinc-copper.

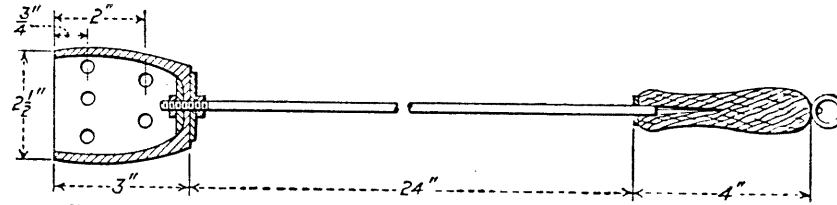


Fig. 7.—Perforated crucible for adding magnesium to alloys. (Rosenhain.)

The properties of three samples in the form of cylindrical rods were as follows: specific gravity, 1.78 to 1.79; Brinell hardness (1-mm. ball, 10 kg.), 48 to 63; yield point, 17,000 to 26,900 lb. per sq. in.; tensile strength, 36,100 to 41,200 lb. per sq. in.; elongation, 13 to 19 per cent; specific tenacity, 250 to 284; yield point in compression, 6700 to 18,800 lb. per sq. in.; and compressive strength, 50,000 to 53,500 lb. per sq. in.

About twenty years ago, 87:13 magnesium-copper alloy was employed considerably for pistons in Germany, while the 90:10 magnesium-copper alloy was used somewhat. The 90:10 magnesium-aluminum, 88:12 magnesium-aluminum, and the 90:8:1:1 magnesium-aluminum-copper-cadmium alloys have all been chill-cast for pistons, while the 89:10:1 magnesium-aluminum-silicon alloy has been used for piston-bin bushings. The 87:13 magnesium-copper alloy, sand-cast, has a tensile strength of about 20,000 lb. per sq. in., 1.5 per cent elongation, and 55 Brinell hardness number. Other alloys that have been employed include the 90:5:5 magnesium-aluminum-zinc alloy (for aircraft castings) and the 99:1 magnesium-silicon alloy (for pistons). Certain of the magnesium-base alloys are heat-treatable, *e.g.*, magnesium-aluminum. The heat-treatment of such alloys, as in the case of aluminum alloys, depends on the retention in solid solution of a soluble constituent by quenching and its subsequent precipitation in finely dispersed particles by aging. Thus, a heat-treatable magnesium-aluminum alloy may be quenched from 425°C. and aged at 200°C. to cause precipitation of the Mg_3Al_2 . Certain intermediate alloys, *e.g.*, 50:50 and 20:80 magnesium-copper, have been used for deoxidizing in nonferrous practice, and the 69:31 aluminum-magnesium alloy has been employed for mirrors under the name "mirror metal."

In general, the magnesium-aluminum-zinc alloys are far superior to the magnesium-aluminum alloys. As the zinc may run from 1/2 to 3 per cent, and the aluminum from 6 to 10 per cent, the scrap problem is greatly complicated if several alloys are in simultaneous production, and this has apparently militated against their use in the United States.

Alloys of Mg 91 1/2:Al 8:Zn 1 1/2 and Mg 90:Al 9 1/2:Zn 1 1/2 are superior for founding practice. Alloys with 6 Al and 1/2 Zn or with 2 per cent Mn are good extruding alloys; the 8 Al, 1/2 Zn is very poor for this use. While the manganese alloys are superior in corrosion resistance, they are below the aluminum-magnesium alloys in strength.

The usual nomenclature and general properties of the alloys currently used in the United States are given in Tables 3 and 4.

The H alloy (American 4) is apparently a favorite German alloy. It is tough, but inclined to porosity. The Germans also use 3 Al:1 Zn; 4 Al, 3 Zn; 8 1/2 Al: 1/2 Zn; and 9 1/2 Al: 1/2 Zn.

The alloy of magnesium with 8 1/2 Al:3 1/2 Zn is said to give an ultimate tensile strength of 15 to 18 tons per sq. in. after heat-treatment.

As a matter of fact, all magnesium castings should be heat-treated for about 6 hr. at 840°F., and a protective gas must be used in the oven. About 1/2 to 1 per cent sulphur dioxide in the furnace atmosphere gives the castings ample protection. The

TABLE 3.—MAGNESIUM ALLOY SPECIFICATION EQUIVALENTS¹

Type	Basic Magnesium, Inc., alloy	A.S.T.M.		Navy Bureau Aeronautics		Army Air Corps specification	Dow Chemical Co. Dow-metal alloy	American Magnesium Corp. alloy
		Alloy No.	Specification	Alloy No.	Specification			
Casting: Sand casting.....	BMI-4	4	B-80-41T*	4	M-112	57.74-10	H	AM-265
	BMI-11	11	B-80-41T*	11	M-112	M	AM-403
	BMI-17	17	B-80-41T*	17	M-112	C	AM-260
	BMI-A8* BMI-AZ91*							
Die casting.....	BMI-13	13	B-94-40T*	..	M-369	11319	R	AM-263
	BMI-A8* BMI-AZ91*							
	BMI-A8* BMI-AZ91*							
Permanent mold....	BMI-A8* BMI-AZ91*							
	BMI-AZ85*	9	B-107-41T					
	BMI-8	8	B-107-41T	8	M-126	11320	J	AM-57-S
Wrought: Extrusions.....	BMI-11	11	B-107-41T	11	M-126	11320	M	AM-3-S
	BMI-AZ85*	9	B-91-41T					
	BMI-8	8	B-91-41T	J	AM-57-S
Forgings.....	BMI-9	9	B-91-41T	11321	O	AM-58-S
	BMI-8	8	B-90-41T					
	BMI-11	11	B-90-41T	11	M-111	11317	M	AM-3-S

¹ Courtesy Basic Magnesium, Inc.

* These alloys are similar to the English and German alloys of these numbers.

† These specifications are for the castings themselves. The ingot specifications are B-93-41T.

TABLE 4.—MAGNESIUM ALLOYS IN COMMON USE

Alloy	Dow metal	Use	Allowable impurities							Strength as cast, tons per sq. in.			
			Al	Tn	Mn, min.	Si, max.	Cu, max.	Fe, max.	Ni, max.		Pb, max.	Total other, max.	
2													
B93-41T	G	SC	9.4-10.6		0.13	0.02	0.01	0.02	0.001	0.001	0.20	0.30	8.9
		SC	9.4-10.6		0.13	0.20	0.04		0.020		0.30		
4 ^a													
B93-41T ^b	H	SC	5.5-6.5	2.7-3.3	0.18-0.50	0.02	0.01		0.001	0.001	0.10	0.30	12.1
B90-41T		SC	5.5-6.5	2.7-3.3	0.18	0.20	0.04		0.020	0.020	0.30	0.30	
Grade A ^c		SC	5.3-6.7	2.5-3.5	0.15	0.30	0.05		0.010		0.30	0.30	
8 ^d													
B90-41T ^d	J	ES	5.8-7.2	0.5-1.5	0.17	0.02	0.01	0.02	0.001	0.001	0.10	0.30	18.7
B91-41T ^d		S	5.8-7.2	0.4-1.5	0.15	0.30	0.05		0.030		0.30	0.30	
B107-41T ^d		F	5.8-7.2	0.4-1.5	0.15	0.30	0.05		0.020	0.030	0.30	0.30	11.6
		E	5.8-7.2	0.4-1.5	0.15	0.30	0.05		0.030	0.001	0.30	0.30	
9													
B107-41T		F	7.8-9.2	0.2-0.8	0.15	0.30	0.05		0.030		0.30	0.30	
B91-41T		F											
B91-41T		F											
Grade C ^e	O	F	8.0-10.0	0.50									13.4
11													
B93-41T ^b	M	SC			1.3	0.01	0.01		0.001		0.20		
B90-41T		ES			1.3	0.01	0.01		0.001		0.20		
B107-41T		SC			1.2	0.10	0.04		0.020		0.20		
Grade B ^f		S			1.2	0.30	0.05		0.020		0.30		
		E			1.2	0.30	0.05		0.030		0.30		
		SC			1.2	0.30	0.05		0.010		0.20		
13 ^g													
B-94-40T	R	D	8.5-9.5	0.5-0.9	0.15	0.02	0.01	0.02	0.001	0.001	0.10	0.30	
Grade I ^h		D	8.3-9.7	0.4-1.0	0.13	0.05	0.05		0.030		0.30	0.30	
17 ⁱ		D	8.0-11.0	1.0 max.	0.10	1.0	0.05		0.030		0.30	0.30	
B91-41T	C	SC, PM	8.5-9.5	1.7-2.3	0.13	0.02	0.01	0.02	0.001	0.001	0.10	0.30	10.3
Grade C ^j		SC	8.3-9.7	1.7-2.3	0.10	0.20	0.04		0.020		0.30	0.30	

TABLE 4.—MAGNESIUM ALLOYS IN COMMON USE.—(Continued)

Alloy	Dow metal	Use	Allowable impurities							Strength as cast, tons per sq. in.			
			Al	Tn	Mn, min.	Si, max.	Cu, max.	Fe, max.	Ni, max.		Pb, max.	Total other, max.	
18 ^k													
B90-41T ^d		ES	2.4-3.0	0.8-1.3	0.22	0.02	0.01	0.02	0.001	0.001	0.20	0.30	
B91-41T ^d		S	2.4-3.0	0.7-1.3	0.20	0.30	0.05		0.030		0.30	0.30	
B107-41T ^d		F	2.4-3.0	0.7-1.3	0.20	0.03	0.05		0.030		0.30	0.30	
A8 ^l		E	2.4-3.0	0.7-1.3	0.20	0.30	0.05		0.030		0.30	0.30	
			7.6-8.5	3.5 max.	0.5 max.	0.10	0.02	0.02	0.002		0.30	0.30	
A231													
A2285			7.8-9.2	0.2-0.8	0.15	0.30	0.05		0.03		0.30	0.30	
A2855			7.5-8.5	0.4-0.65	0.15-0.25	0.10	0.02	0.02	0.002		0.30	0.30	
A291			9.5-10.5	0.4-1.0	0.5 max.	0.4	0.4	0.01			1.0	0.30	
AZG			6.0	3.5	0.5	0.4	0.4	0.01			0.30	0.30	
DTD-59A	SC		8.5	3.5									
DTD-88B	F		6.0-8.0	0.5									
DTD-289			8.5	0.5									
DTD-142					2.0								

NOTES: SC, sand casting; PM, permanent mold casting; D, die casting; E, extrusion; F, forging; S, sheet, strip or plate.

^a 4X—Fe, 0.003; Ni, 0.0036.

^b Ingot specifications for casting.

^c Grades A, B, and C are defined by Specifications AN-QQ-M50, a fabricated product specification.

^d Finished product specifications.

^e 8X—Fe, 0.005; Ni, 0.005.

^f 13X—Fe, 0.003; Ni, 0.003.

^g Grade I is defined by A.A.F. specifications 11310.

^h A8X—Fe, 0.005.

ⁱ 17X—Fe, 0.003; Ni, 0.003.

treatment for 6 hr. at 840°F. may be considered a minimum. E. F. Cone recommends 12 hr. at 715 to 730°F. for solution and 16 hr. additional at 350°F. for aging[56].

Magnesium is a constituent of certain aluminum alloys, *e.g.*, duralumin, zinc duralumin, magnaliums, and so-called Y-alloy of the National Physical Laboratory (92.5:4:1.5:2 aluminum-copper-magnesium-nickel). Magnesium is present in duralumin and zinc duralumin in an amount of 0.5 to 1.0 per cent, and by the formation of magnesium silicide, Mg_2Si , is largely responsible for the duralumin phenomenon. Magnaliums are aluminum-rich alloys containing magnesium up to 10 per cent and magnesium with other elements.

Melting and Casting.—Magnesium alloys are more difficult to prepare than are aluminum alloys. In practice, the magnesium is usually melted in cast iron or steel pots fired by oil or gas and the alloys with aluminum and with zinc are made simply by adding definite amounts of solid metals to liquid magnesium. Manganese is preferably added by using a flux that contains manganese chloride, the manganese being reduced by the magnesium. The Dow Chemical Co. has two such fluxes; its No. 250 (melting) consists of 23KCl, 72MgCl₂, 2½BaCl₂, and 2½CaF₂. This flux is usually used following a refining with the Dow No. 230 flux, which is a general open-pot flux consisting of 55KCl, 34MgCl₂, 9BaCl₂, and 2CaF₂. The Dow Chemical Co.'s No. 320 is another flux used for the introduction of manganese. This contains 76MnCl₂, 13CaF₂, and 11MgO. This is used after a refining with No. 310 flux, which consists of 20KCl, 50MgCl₂, 15CaF₂, and 15MgO.

The British refining fluxes used where we use the Dow 320 and 230 are MgCl₂, 30; NaCl, 30; KCl, 30; and MgF₂, 10, or less commonly MgCl₂, 39; CaCl₂, 15; NaCl, 7; KCl, 7; CaF₂, 20; MgO, 12.

A flux recommended by Dow Chemical for refining metal in a covered pot provided with SO₂ surface protection is No. 220, 57KCl, 28CaCl₂, 12½BaCl₂, and 2½CaF₂. This flux is removed after refining. A British flux used for melting is MgCl₂, 33; CaCl₂, 30; NaCl, 15; KCl, 15; and MgO, 1.

There are various other fluxes on the market that appear to be mixtures of the various chlorides and fluorides already mentioned, and some appear to contain borates and boric acid and sulphur. Schreiber and Beck[17] patented the use of sulphur as a flux, the idea being to cause a layer of sulphur vapor to float above the liquid metal, while above that was a layer of sulphur dioxide from the combustion of this vapor. Veazey and Burdick[12] and Gann[13] held patents for various halide mixes, but these patents have now expired. Oxidation on melting has been discussed by de Fleury[31] in a paper that is still a classic.

The older workers recommended that magnesium or its alloys should not be heated to a temperature exceeding 1350°F., but it appears that a superheating (say 15 min.) at 1650 to 1750°F. refines the grain of aluminum alloy. However, if this is given, it is important that the metal be brought down to pouring temperature and poured with little delay. The grain refinement is rapidly lost on standing at pouring temperatures (say around 1450°F.)

Magnesium cannot be poured into green sand (water-tempered) molds since it reacts with the moisture. For green-sand molds with magnesium, the usual water is replaced with kerosene, glycerine, or ethylene glycol, which prevents ignition of the hot metal. A sand of 1G to 2G grade should be used.¹ An exception to the above is in the use of synthetic sands [such a mixture is silica sand (minus 40 mesh), 91 per cent; boric acid, ½ per cent; sulphur, 4½ per cent; bentonite, 4 per cent]. This mixture has been successfully employed, using about 3½ per cent of water for mixing. Cores may be bonded with dextrin, corn oil, or sodium silicate solution and baked.

¹ The American Foundrymen's Association is using the following classification for foundry sand. Clay content is denoted by letter:

The synthetic sand mentioned above may be used for cores, but in this case the sand is a little coarser than 40 mesh, and a little less sulphur is used. Some authorities recommend a dusting of the mold with bentonite or graphite. The sand for magnesium-alloy casting should be permeable and the molds freely vented. Magnesium cannot be poured directly into molds; some device such as a pouring cup must be used to break the fall of the metal, so as to reduce the amount of air carried into the mold as greatly as possible. A current of nitrogen or chlorine gas flowing through the molds is sometimes recommended to reduce the porosity of the castings, but does not appear to be necessary. Gates and risers of great size must be used; in fact, the gates and risers may weigh two and one-half to three times what the casting does from which they are cut off[64].

Precipitation of Iron.—There is a tendency for iron to be introduced into magnesium alloys through the magnesium itself, from the iron pickup in remelting magnesium scrap, from the aluminum, from the flux, and from the crucible itself. If manganese is introduced by the use of manganese chloride or the Dow 250 or 320 flux, spoken of above, to the saturation point during the superheating to produce grain refining, the iron is precipitated to the bottom of the crucible on reducing to the pouring temperature. The iron contents may be reduced to 0.001 per cent by this process. Any attempt to remelt or reheat such high-purity alloys appreciably above 1300 to 1350°F. in steel crucibles will inevitably lead to recontamination by iron.

A sand—	0 up to but not including	0.5 per cent clay
B sand—	0.5 and up to but not including	2.0 per cent clay
C sand—	2.0 and up to but not including	5.0 per cent clay
D sand—	5.0 and up to but not including	10.0 per cent clay
E sand—	10.0 and up to but not including	15.0 per cent clay
F sand—	15.0 and up to but not including	20.0 per cent clay
G sand—	20.0 and up to but not including	30.0 per cent clay
H sand—	30.0 and up to but not including	45.0 per cent clay

The fineness is then expressed by a series of arbitrary numbers, derived as follows: The sand, freed from clay, is screened, and the residues on the screens expressed as per cents are multiplied by the following factors:

	On 6 mesh ×	3
Through 6, on	12 mesh ×	5
Through 12, on	20 mesh ×	10
Through 20, on	30 mesh ×	20
Through 30, on	40 mesh ×	30
Through 40, on	50 mesh ×	40
Through 50, on	70 mesh ×	50
Through 70, on	100 mesh ×	70
Through 100, on	140 mesh ×	100
Through 140, on	200 mesh ×	140
Through 200, on	270-mesh ×	200
Through 270 mesh		× 300

The products of these multiplications are then added and divided by the total percentage of sand, *i.e.*, the clay is excluded. The sand is then classified according to the quotient thus obtained.

No. 1 sand corresponds to	quotients from 200–300
No. 2 sand corresponds to	quotients from 140–199
No. 3 sand corresponds to	quotients from 100–139
No. 4 sand corresponds to	quotients from 70–99
No. 5 sand corresponds to	quotients from 50–69
No. 6 sand corresponds to	quotients from 40–49
No. 7 sand corresponds to	quotients from 30–39
No. 8 sand corresponds to	quotients from 20–29
No. 9 sand corresponds to	quotients from 10–19

From "Standards and Tentative Standards for Testing and Grading Foundry Sands," American Foundrymen's Association, July, 1938.

As indicated previously, magnesium is used to a considerable extent as a deoxidizer in nonferrous foundry practice. It is also a minor alloying element or a constituent in subordinate amount in certain alloys. For making fixed additions of magnesium, it is advisable not to add the entire amount at once by simply throwing the metal into a liquid melt, but small pieces may be pushed under the surface by tongs and held until dissolved. If thrown into a liquid melt, the magnesium will break up, float on the surface, and burn. A useful device for making fixed additions of magnesium is a form of "phosphorizer," such as is used in adding phosphorus to alloys. The tubular device of Naylor and Hutton (U.S. patent 1475055) is useful, or the perforated crucible [16] shown in Fig. 7 may be employed.

Impregnation of Magnesium Castings.—Even with the utmost care, there is a decided tendency for magnesium castings to be porous. This tendency can be corrected to some extent by impregnating the castings with tung oil or with sodium silicate solution under pressure. In the case of sodium silicate, the casting has to be thoroughly cleaned, or unsightly stains result. Tung oil seems to be the better reagent, though it has been difficult and sometimes impossible to get under war conditions. Pressures up to 200 lb. per sq. in. and temperature up to 475°F. are often used. This, of course, necessitates carrying the process on in an autoclave.

Anodizing.—Consolidated Vultee Aircraft Corporation has recently announced that it has a corrosion- and abrasion-resisting finish, produced by anodizing in an alkaline solution, which will apparently be made generally available to industry. Except that it requires a fairly close temperature control (from 171 to 179°F.), no details have been given out.

Mechanical Treatment.—Both magnesium and certain magnesium-rich alloys can be readily rolled hot and to some extent cold, but when rolled cold frequent annealings are necessary between passes in order to avoid cracking. Both the metal and magnesium-base alloys containing, for example, up to 10 per cent aluminum or zinc are worked (rolled or forged) at 350 to 400°C., and extruded at 550°C. The ordinary ribbon is made by pressing the semifluid metal into wire and then flattening it. The powder is made by disintegrating the metal in the pasty condition, or by milling. Magnesium and its alloys are soldered with great difficulty, but welding is done similar to aluminum welding. The use of a slightly reducing oxyacetylene flame and fluoride fluxes is recommended. Both magnesium and magnesium alloys may be machined very rapidly and easily, and the machinability of magnesium is unexceeded by any other metal. It exhibits no dragging tendency as does aluminum, and all machine-tool operations can be carried out much faster than on aluminum and its alloys. Welding is also carried on, using a hollow electrode through which helium is passed to give a neutral atmosphere.

Metallography.—Magnesium has a hexagonal close-packed lattice, with lattice parameter $a = 3.22$ and $c = 5.23$ (axial ratio 1.624). Magnesium does not work well because of its crystal structure. The ductile and malleable metals (like aluminum) have face-centered cubic lattices. The constitution and metallography of many binary systems of magnesium with other metals have been examined, and the diagrams of thermal equilibrium published [25]. Magnesium and its alloys may be etched satisfactorily with dilute acids, e.g., acetic acid and nitric acid. A solution of 1 per cent hydrochloric acid plus 0.5 per cent nitric acid in alcohol is also a satisfactory etching reagent.

Selected Bibliography.—The literature on magnesium in general, particularly the chemical side, is large. A few of the more important references are given below.

1. LEJEAL, A.: "L'aluminium, le baryum, le strontium, le calcium, le manganèse, et le magnésium," J. B. Ballière et fils, Paris, 1894.

2. TUCKER, A. E., and F. L. JOUARD: The Electrolytic Preparation of Magnesium, *Trans. Am. Electrochem. Soc.*, Vol. 17, pp. 249-260, 1910.
3. EGER, G.: Studie über die Konstitution der ternären Magnesium-Aluminium-Zink Legierungen, *Intern. Z. Metallog.*, Vol. 4, pp. 29-126, 1913.
4. GROSVENOR, W. M.: Magnesium, *Trans. Am. Electrochem. Soc.*, Vol. 29, pp. 521-526, 1916.
5. HESS, F. L.: "Magnesium," "Mineral Resources of the U. S.," volume for 1915, part 1, "Metals," pp. 735-741; *U. S. Geol. Survey*, 1917, and later reports by STONE, LOUGHLIN, and HILL.
6. Japanese patent 42439, Apr. 29, 1922.
7. U. S. patent 1408141, and 1408142, Feb. 28, 1922; and Norwegian patent 30873, July 5, 1920.
8. U. S. patent 1533911, Apr. 14, 1925.
9. U. S. patent 881934, Mar. 17, 1908.
10. PHALEN, W. C.: "Notes on the Magnesium Industry in the United States," *U. S. Bur. Mines Repts. Investigations*, May, 1920, 11 pp.
11. British patent 173742, Dec. 7, 1921.
12. U. S. patent 1476192, Dec. 4, 1923.
13. U. S. patents 1519128, Dec. 16, 1924, and 1534105, Apr. 21, 1925.
14. FLUSIN, G.: Le magnésium, le calcium, et le sodium, *Rev. mét.*, Vol. 18, pp. 586-589, 1921; and *Bull. soc. encour. ind. nat.*, Vol. 133, pp. 787-812, 1921.
15. BECKINSALE, S.: The Magnesium Alloy Electron, *Jour. Inst. Metals*, Vol. 26, pp. 375-376, 1921.
16. ROSENHAIN, W., S. L. ARCHBUTT, and D. HANSON: Eleventh Report to the Alloys Research Committee—On Some Alloys of Aluminum (Light Alloys), Institute of Mechanical Engineers, August, 1921.
17. U. S. patent 1540867, June 9, 1925.
18. ALLEN, S. T.: The Production of Metallic Magnesium, *Electrician*, Vol. 88, pp. 92-93, 1922; and abstracted *Chem. & Met. Eng.*, Vol. 26, pp. 987-988, 1922.
19. BOYNTON, K. S., V. LANGFORD, and J. F. G. HICKS: Electrolytic Recovery of Magnesium from Salt Works Residues, *Jour. Ind. Eng. Chem.*, Vol. 14, pp. 146-147, 1922.
20. MATIGNON, C., and J. VALENTINE: Diagrammes de solidification du système MgCl-KCl-BaCl₂, *Bull. soc. chim.*, Vol. 33, pp. 267 et seq., 1923.
21. FEDOTIEFF, P. P.: Die technische Elektrolyse des geschmolzenen Karnallite, *Z. anorg. Chem.*, Vol. 130, pp. 25-38, 1923.
22. EDWARDS, J. D., and C. S. TAYLOR: Density of Magnesium from 20 to 700°C., *Trans. A.I.M.E.*, Vol. 69, pp. 1070-1074, 1923.
23. CZENTNERSZWER, M.: Velocity of Dissolution of Magnesium in Acids, *Rec. trav. chim.*, Vol. 42, pp. 1065-1073, 1923.
24. MOORE, R. R.: Resistance of Manganese Bronze, Duralumin and Elektron Metal to Alternating Stresses, *Proc. A.S.T.M.*, Vol. 23, Part II, pp. 106-109, 1923.
25. Anonymous: Magnesium, handbook published by American Magnesium Corp., Niagara Falls, N. Y.
26. SMITS, A.: The Electromotive Behavior of Magnesium, *Proc. Acad. Sci., Amsterdam*, Vol. 26, pp. 395-407, 1923; and Das elektromotorische Verhalten des Magnesiums, *Z. Elektrochem.*, Vol. 30, pp. 223-230, 1924.
27. MEHL, R. F.: The Preparation of Pure Alloys, *Trans. Am. Electrochem. Soc.*, Vol. 46, pp. 149-176, 1924.
28. MIYAKE, M. and A. BUTTS.: Metallurgy of Magnesium, *Eng. Mining Jour.-Press*, Vol. 119, pp. 843-846, 1925. (Gives bibliography.)

29. MOORE, R. R.: Some Fatigue Tests on Non-ferrous Metals, paper before the A.S.T.M., Atlantic City meeting, June, 1925.
30. HARVEY, W. G.: Production of Metallic Magnesium from Fused Salts, paper before the American Electrochemical Society, Niagara Falls meeting, April, 1925, and see *Chem. & Met. Eng.*, Vol. 32, pp. 573-576, 1925.
31. DE FLEURY, R.: Some Notes on the Founding of Light Alloys, paper before the American Foundryman's Association, Syracuse meeting, October, 1925; French exchange paper, translation by R. J. Anderson.
32. GANN, JOHN A.: Magnesium, Reviewing Its Technology of Production and Use, *Mining Met.*, April, 1932.
33. TALBOT, A. M., and JOHN T. NORTON: Age Hardening of Magnesium-aluminum Alloys, *Metals Tech.*, February, 1936.
34. PIDGEON, L. M., and N. W. PHILLIPS: The Production of Anhydrous Magnesium Chloride, *Trans. Electrochem. Soc.*, Oct. 7, 1940.
35. HOUSTON, E. C., and H. S. RANKIN: Olivine As a Source of Magnesium Chloride, *Trans. A.I.M.E. Tech. Paper* 1484, October, 1941.
36. Anonymous: Magnesium, *Mining Met.*, October, 1941.
37. PAWEL, GEORGE W.: Olivine: Potential Source of Magnesia, *Mining Met.*, June, 1942.
38. Anonymous: Magnesium Becomes a Major Metal, *Mining Met.*, December, 1942.
39. Anonymous: New Deal for Basic Magnesium, *Mining Met.*, January, 1943.
40. WILSON, PHILIP D.: Magnesium: Production and Technology, *Mining Met.*, February, 1943, pp. 70-72.
41. DESCH, C. H.: Magnesium in Modern Metallurgy, *Metal Treatment*, Vol. 10, pp. 35-46, 1943. A lecture.
42. PANNELL, E. V.: "Magnesium, Its Production and Use," Sir Isaac Pitman & Sons, Ltd., London, 1943. A complete treatise.
43. SPELLMIRE, WALTER B.: *Gen. Elec. Rev.*, Vol. 46, pp. 372-376, 1943. A general review of the subject.
44. MANNING, PAUL D. V.: Magnesium—Its Sources, Methods of Reduction and Commercial Applications, *Mining Met.*, August, 1943, pp. 346-349.
45. U. S. patents 2313753, 2313754, 2313755, 2313756.
46. PIDGEON, L. M.: Production of Magnesium, *Can. Chem. and Process Industries*, Vol. 23, pp. 395-400, August, 1939.
47. ALTWICKER, H.: "Magnesium und seine Legierung," Julius Springer, Berlin, 1939. A translation of this was published by F. A. Hughes & Co., London, 1940, under the title "Technology of Magnesium and Its Alloys."
48. PITAVAL, R.: Le magnésium, métal de guerre, *Jour. Jour élec.*, Vol. 49, p. 111, 1940.
49. DOERNER, H. A.: Magnesium by Electrothermic Reduction, *Mining Congr. Jour.*, Vol. 27, p. 42, 1941.
50. PANNELL, ERNEST V.: How Europe Produces Its Magnesium, *Chem. & Met. Eng.*, Vol. 48, pp. 75-77, March, 1941.
51. KIRKPATRICK, S. D.: Magnesium by the Hansgirg Process, *Chem. & Met. Eng.*, Vol. 48, pp. 91-94, September, 1941.
52. FRANKS, HERBERT A.: Magnesium, Its Production and Use, *Chem. & Met. Eng.*, Vol. 48, pp. 75-77, March, 1941.
53. DE LONG, H. K., and W. H. GROSS: Surface Treatment for Magnesium, *Iron Age*, Vol. 150, pp. 68-69, July 2, 1942.
54. BREYER, F. A.: Pidgeon Ferro-silicon Process for Magnesium, *Chem. & Met. Eng.*, Vol. 49, p. 87, Apr. 4, 1942.
55. WILSON, PHILIP D.: Magnesium, *Mining Met.*, February, 1944, p. 74.
56. CONE, EDWIN F.: The Ford Magnesium Foundry, *Metals & Alloys*, Vol. 15, p. 401.

57. Anonymous: Magnesium by the Ton, *Fortune*, March, 1944, p. 157.
58. DUNGAN, T. A.: Production of Magnesium by the Carbothermic Process at Permanente, *A.I.M.E., Tech. Pub.* 1671, February meeting, 1944.
59. PEIRCE, W. M., R. K. WARING, L. D. FETTEROLF, and G. T. MAHLER: Some Developments in the Production of Magnesium from Dolomite by the Ferrosilicon Process, *A.I.M.E., Tech. Pub.* 1707.
60. NELSON, C. E.: The Melting and Refining of Magnesium, *A.I.M.E., Tech. Pub.* 1708.
61. MAYER, ANDREW: Plant for the Production of Magnesium by the Ferrosilicon Process, *A.I.M.E., Tech. Pub.* 1670.
62. FOLEY, F. B., and R. L. SEBASTIAN: Cast Retorts for Magnesium Distillation at 2150°F. by the Pidgeon Process, *A.I.M.E. Tech. Pub.* 1709.
63. RAMSEY, R. H.: The Why and How of Basic Magnesium, *Eng. Mining Jour.*, pp. 61-67, October, 1943.
64. MYERS, O. J.: Oxidation Inhibitors in Core-Sand Mixtures for Magnesium Castings, *Metals Tech.*, February, 1945.

BERYLLIUM¹

Sources.—From a commercial standpoint, the only beryllium mineral now warranting attention is beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, which is of fairly widespread occurrence. The chief deposits are in Brazil, Argentina, India, Canada, and Portugal. When pure this contains about 14 per cent beryllium oxide. The mineral richest in beryllium is phenacite, $(\text{BeO})_2\text{SiO}_2$, or beryllium orthosilicate, which contains 45.55 per cent beryllium oxide when pure. If anyone is ever fortunate enough to discover a large deposit of it, it will revolutionize beryllium metallurgy.

Gadolinite, $2\text{BeO} \cdot \text{FeO} \cdot 2\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$, is often referred to as a beryllium mineral, though the occurrences are comparatively scant and it is of more interest as a source of yttrium than it is of beryllium.

There has been a good deal of talk recently regarding some occurrences of helvite occurring in the United States. Helvite is a complex manganese-iron beryllium silicate, and apart from difficulties that would arise in its treatment because of its composition, the beryllium content of the known deposits is not high.

Early Metallurgy.—The element beryllium was first isolated by L. N. Vauquelin in 1797.² He crushed and heated beryl, having the idea that this heating made the mineral more readily amenable to attack by chemicals, and then mixed the mineral with three times its weight of caustic potash and fused the mixture. The melt after cooling was dissolved in hydrochloric acid, dehydrated, and again taken up with hydrochloric acid and filtered to separate the silica. The filtrate was treated with an excess of potassium carbonate, and the precipitate after draining was leached with a solution of caustic potash which dissolved the alumina. The undissolved material was, in Vauquelin's own words, *une terre nouvelle*. He dissolved this precipitate with nitric acid and evaporated to dryness, took up with hydrochloric acid and threw the iron out with potassium hydrosulphide, though he found that to make a complete separation of the iron involved a second treatment. The solution after throwing out the iron had a pronounced sweet taste, and though Vauquelin always speaks of working on *terre du béril* he suggests that the new element should be known as "glucine" (glucinum) from the Greek word for sweet, because of this outstanding property.

Vauquelin did considerable work on the comparison of aluminum and beryllium, working out a separation of most of the aluminum based on its precipitation as alum.

¹ An abridgement of this section, by the editor, appears in the Non-Ferrous Metallurgy volume of the American Institute of Mining and Metallurgical Engineers.

² *Ann. chim. phys.*, Vol. 26, pp. 115-179, 1798.

His work is reviewed at some length, since ordinarily his procedure is incorrectly set forth in modern metallurgical works. It will also be recognized by those who have studied beryllium metallurgy that a good many technicians have followed his ideas since, including preheating the beryl before treatment, which has even been allowed as an invention in recent patent claims. The fusion with caustic alkali has been done by H. N. Warren (1894), G. Wyruboff (1902), J. H. Pollok (1903), C. L. Parsons and Barnes (1906), F. Bran and G. Van Ordt (1907), L. Petit-Devaucelle (1926), and C. F. Brush, H. Fischer, H. H. Armstrong, G. Jaeger, and C. Adamoli, to cite only those processes immediately occurring to the author. R. H. McKee worked with alkalies in solution in an autoclave, rather than by fusion.

Vauquelin also proved the existence in the emerald of the same new element that he had found in beryl.

Humphrey Davy (about 1808) and Wöhler (1827) produced an impure metallic beryllium by reducing the oxide with metallic sodium or metallic potassium.

The first use of alkaline carbonates as decomposition agents came over half a century later. Henri Debray in 1854 pulverized beryl and fused it with half its weight of calcium oxide.¹ The mass obtained by this fusion he powdered and treated with dilute nitric acid until a homogeneous jelly was produced. Then he evaporated the jelly to dryness and calcined until the nitrates of beryllium and iron were decomposed as well as some of the calcium nitrate. This residue he treated with ammonium chloride. Apparently he counted on the evolution of ammonia by the decomposed calcium nitrate to keep most of the iron and alumina in the insoluble residue with the silica. If there was no evolution of ammonia, he argued that he had not carried his calcination far enough. He filtered off the solution of beryllium and calcium and poured the filtrate into an excess of ammoniacal ammonium carbonate solution and allowed the mixture to stand for 7 or 8 days, and then added some ammonium hydro-sulphide to precipitate the iron completely. He then filtered off the pure beryllium solution, which he concentrated by boiling until basic beryllium carbonate separated as a white powder. Again, metallurgists who have worked with beryllium will recognize that Debray's caustic lime decomposition of beryl has formed the basis for at least a dozen metallurgical processes based on this method of attack.

Debray refers at some length to Berthier's work on the separation of beryllium from alumina. Berthier suspended the well-washed mixture of these earths in water and passed in sulphur dioxide until they dissolved, after which he boiled off the excess of sulphur dioxide. Berthier claimed that the alumina precipitated and left the beryllium in solution. Debray thinks it is an inferior separation, although it still figures in some modern patent work.

The first decomposition of beryl with fluorine that the author has found was that of G. Sheffer in 1858, who heated beryl with fluorspar and sulphuric acid, thus driving off the silicon as silicon tetrafluoride.² The excess hydrofluoric acid is also driven off. He leached the residue with dilute sulphuric acid and threw out most of the alumina as an ammonium or sodium alum. The rest of the alumina was thrown out by treating the solution with zinc, which produced an insoluble basic aluminum carbonate. The zinc which had dissolved then had to be in turn removed in part as potassium zinc sulphate and finally as zinc sulphide, the beryllium eventually being precipitated by the use of ammonium carbonate.

John Gibson in 1893 decomposed beryl with ammonium fluoride. This will also be recognized as a precursor of various recent patents. P. Lebeau as early as 1895 described a process based on fusing beryl with twice its weight of calcium fluoride, which he stated could be done at a comparatively moderate temperature. He

¹ *Ann. chim. phys.*, Vol. 54, 3d series, pp. 5-41, 1855.

² *Ann. Chem. Pharm.*, Vol. 33, p. 144-147, 1859.

treated the melt with sulphuric acid, driving off silicon tetrafluoride and hydrofluoric acid.

Lebeau also treated beryl in an electric furnace with an excess of carbon, reducing some of the silica to silicon, which distilled off, and in part reducing it to silicon carbide and ferrosilicon. The aluminum and beryllium were converted into carbides. This electric-furnace product disintegrates by weathering and is easily attacked by sulphuric acid.

In 1915, H. Copaux took out French patent 476475 which is based on fusing beryl with sodium fluosilicate. This process, sometimes with the addition of alkaline hydroxides or carbonates or of sodium fluoride, has since been followed by a number of inventors.

Electric-furnace Processes.—Other metallurgists also worked with the electric furnace. L. Burgess produced beryllium carbide or beryllium silicide in an electric furnace, distilling off beryllium chloride. He also reduced under such conditions as to form tetraberyllium trisilicide and also worked on a method for concentrating beryllium in a scoria by forming ferrosilicon in the furnace, using an insufficient amount of carbon to reduce the beryllium (U.S. patent 1905340 of 1933).

B. R. F. Kjillgren also worked on this idea of the production of ferrosilicon (U.S. patent 2092621 of 1937).

H. Lowenstein based his process on the production of beryllium sulphide, using pyrite as a source of his sulphur and thus sulphurizing the beryllium (U.S. patent 1777267 of 1930).

D. Gardner worked on the production of beryllium sulphide by sulphurizing with carbon disulphide in the presence of an excess of carbon at 1800 to 2000°C. (U.S. patent 2166659 of 1930).

H. H. Armstrong reduced with carbon or CaC₂ at a temperature high enough to volatilize the Si, then leached with H₂SO₄ (U.S. patent 2273168 of 1943).

Reduction to Metal.—Although certain early experimenters following the procedure of Davy and Wöhler claimed to have produced beryllium 99.8 per cent pure, it seems probable that Lebeau was the first to prepare metal of this or higher purity, which he did in 1894 by electrolyzing Na₂BeF₄ at a temperature below red heat, using a nickel crucible to contain the electrolyte. This crucible also served as his cathode. The anode was graphite.

One of the great obstacles to recovering beryllium as the pure metal is its extreme lightness. The slags or scorias produced by chemical reduction are often heavier than the metal so that the metal floats on top of them instead of being protected by them. In the electrolytic production of beryllium, the fused electrolyte is often heavier than the metal, which means that it is difficult to prevent the metal from taking fire at the anode. This lightness of the metal is one of the reasons why it is easier to produce a master alloy of beryllium rather than the pure metal.

Commercial Processes.—In general, modern processes for beryllium production are based on bringing beryllium into solution as an alkaline fluoberyllate as initiated by Copaux or as beryllium sulphate or chloride, usually, in the last-named methods, dissolving the beryllium after a preliminary decomposition of the beryl by an alkaline hydroxide or carbonate or an alkaline-earth oxide or carbonate. High-temperature chlorination has also been resorted to for the direct production of chloride, using chlorine, hydrochloric acid, and carbon tetrachloride or various combinations of them.

The fluoride-recovery processes take various forms, as the fusion with sodium fluosilicate as devised by Copaux spoken of above, or by attack by hydrofluoric acid at high temperatures, or silicon tetrafluoride at high temperatures, or in organic solution; by treatment with ammonium fluoride both as a gas or in solution under pressure; by the use of acid sodium fluoride either under pressure or at high tempera-

ture; and most recent of all by the Kawecki process (U.S. patent 2312297 of 1943) employing sodium iron fluoride (iron cryolite).

All these processes depend on the fact that the alkaline fluoberyllates are soluble in water though beryllium fluoride is not.

As stated above, sulphate solutions are usually prepared after decomposition of the beryl with the alkaline or alkaline-earth hydroxides or carbonates, though Sawyer (U.S. patent 1823864) in 1931 claimed the use of sulphuric acid on the beryl itself after heating to 1000°C. Jaeger and Wille in 1939 (U.S. patent 2160547) claimed that beryl could be decomposed by treatment with sulphuric acid or acid sulphate if a small amount of fluoride was present, stating that only one-tenth of the amount of the costly fluorine radical was necessary in this process that would be required for a complete decomposition of the beryl with fluorine.

One inventor rather dodges his responsibilities by stating that he prepares a sulphate solution "in any well-known manner."

Reduction to Metal.—There is no outstanding method for the reduction of beryllium metal any more than there is any process for the decomposition of beryl that is comparatively unequaled. There are various patents and processes covering the electrolysis of beryllium fluoride or beryllium oxyfluoride, $\text{BeO} \cdot 5\text{BeF}_2$, such as those of Cooper, Zeppelin, Fischer, and Adamoli; for the electrolysis of beryllium fluoride in solution in molten calcium fluoride and in various halide electrolytes, and for the electrolysis of beryllium chloride in electrolytes where the metallic base of the solvent is more electropositive than is beryllium, such as sodium, potassium, or lithium chloride or mixtures of them. The electrolysis of beryllium hydroxide or beryllium chloride in solution in anhydrous ammonia has also been patented by Booth, Torrey, and Merlub-Sobel (U.S. patent 1893221). The use of sodium or potassium to reduce beryllium halides over 100 years ago by various experimenters has already been commented on. Magnesium has also been used to reduce the normal sodium fluoberyllate, Na_2BeF_4 , the monosodium fluoberyllate, NaBeF_3 , and also beryllium chloride. It may be noted in passing that the reduction of chemically pure Na_2BeF_4 by pure magnesium is likely to result in a disastrous explosion. The direct reduction of beryllium oxide by magnesium fails because of the extreme infusibility of the oxide. The reaction quickly comes to a halt because of the lack of contact between the reducer and the material to be reduced.

Beryllium is like aluminum in that reduction by carbon produces a carbide rather than beryllium metal. It likewise resembles aluminum in that the reduction of beryllium and a basic metal for the production of a master alloy can be performed by the use of carbon, which reaction has been patented by Gahagan (2193482) and Gruber and Hessenbruch (2228310). Beryllium can also be produced in the same manner as magnesium by thermal reduction with carbon, the beryllium being volatilized and then condensed. Beryllium can also be reduced by carbon in the presence of hydrogen. Some experimenters have claimed that the hydrogen must be in the atomic form but the writer does not feel sure that this has been proved.

Other properties that make the metallurgy of this element a perplexing problem are the following: the metal has a high fusion point and a high vapor pressure at a temperature of not much above the fusion point; the pure metal is exceedingly light and has a tendency to float on slags and on fused electrolytes; the halides are all highly deliquescent, and after they have absorbed water from the air, they cannot be recon-verted to an anhydrous salt by simple heating, as all the halides hydrolyze readily; when beryllium hydroxide is precipitated, it has a tendency to occlude and adsorb other salts and there is also a tendency to form basic and oxy-salts. In short, beryllium deserves the characterization given it by Dr. C. B. Sawyer, of being "the world's No. 1 metallurgical headache."

Perosa Process.—While it would be possible for anyone to construct his own flow sheet from the information that has already been given, it may be of interest to follow in detail the recovery of the metal by the Perosa process.

The beryl is heated and is then crushed and ground so that 100 per cent passes 100 mesh. It is then mixed with acid sodium fluoride in the proportion of 4 atoms of fluorine to 1 atom of beryllium, and this mixture is briquetted. The beryllium is converted to sodium fluoberyllate when the briquettes are sintered at 650 to 800°C. The sintered briquettes are crushed and ground and leached with hot water. The filtered solution is then purified from iron, manganese, and alumina by being made exactly neutral by the addition of sodium hydroxide, and a little potassium permanganate is added. The iron-manganese-alumina precipitate is filtered off, and an excess of sodium hydroxide added to the solution. Beryllium hydroxide is precipitated, which is filtered off, washed, and dried. The drying temperature should not exceed the decomposition temperature of the hydroxide by more than a few degrees; for if it is dried at too high a temperature, its reactivity becomes less than if it is dried close to its decomposition point. After drying, the material is ground in a paint mill with acid ammonium fluoride, which converts the hydroxide to ammonium beryllium fluoride. The ammonium-beryllium fluoride is then briquetted and heated at a temperature sufficiently high to drive off the ammonium fluoride, leaving pure beryllium fluoride behind. This beryllium fluoride is then reduced with magnesium or a magnesium alloy in the presence of some of the metal of which it is desired to form a master alloy.

Because of the high cost of fluorine, no matter what the form in which it is obtained, the solution from the precipitation of the beryllium hydroxide must be treated to recover fluorine, as must also the slags from the final reduction.

Uses of Beryllium.—Except for alloying purposes, the metal has no great value. The greatest use of beryllium is in the production of alloys with copper. These alloys require proper heat-treatment to bring out their best characteristics, this heat-treatment being covered by U.S. patents 1975112 and 1975113 issued to Masing and Dahl, rights to which are held by the Beryllium Co. of America. When properly heat-treated the alloys, particularly in the range 2.3 to 2.6 beryllium, develop a tensile strength comparable to good steel with a fatigue limit which far exceeds that of many steels. The beryllium-copper alloys, even when the beryllium is in small quantity, have a high resistance to many forms of chemical corrosion.

Some of the beryllium-nickel alloys, particularly those approximating 4 per cent Be, 96 per cent Ni, also have an amazing resistance to corrosion and have fine mechanical properties. It is understood that these alloys have been used to a considerable extent for surgical instruments by the Germans.

The supply of beryllium has been insufficient during the war to meet even the demands for master alloys to make cuproberyllium, nickel-beryllium, and some other alloys for military use. There has been some interesting work done on light alloys of magnesium, aluminum, and beryllium stabilized with at least two other elements and employing fairly high percentages of beryllium (in the neighborhood of 22 to 25 per cent). Whether these alloys will find any commercial use after the war will have to wait until it can be seen what the beryllium supply will be and what will be taken by the low-percentage uses.

Determination of Beryllium.¹—The ore, usually beryl, should be ground until 100 per cent passes 100 mesh. Fuse 0.5 g. of the ground ore with potassium sodium carbonate in a platinum crucible, for at least 20 min.

¹ Courtesy Lucius Pitkin & Co., New York.

Transfer the melt to a porcelain casserole, and dissolve in HCl. Evaporate to dryness on a water bath, repeating the evaporation with HCl to ensure dehydration of the silica. After the second evaporation, bake in a hot plate.

Filter off the insoluble residue, dry and ignite in a platinum crucible, then treat the residue with HF and H₂SO₄ until the silica is expelled. Fuse the silica-free residue in platinum with HKSO₄, and dissolve the melt, filter, and add the filtrate to the main solution.

The solution is made slightly ammoniacal and the excess ammonia boiled off. Filter, redissolve the precipitate in HCl, and reprecipitate with NH₃.

Evaporate the united filtrates to fumes with an excess of sulphuric acid, dissolve in water, filter, and once more treat with ammonia. If there were fluorides in the original sample, more NH₃ precipitate will form. Add it to the main NH₃ precipitate, if it does.

Dissolve the hydroxide precipitate in 5 to 10 cc. of HCl, and dilute the solution to about 400 cc. Make barely ammoniacal, and then make barely acid with HCl.

Then, while stirring, add an excess of hydroxyquinoline solution (5 per cent in 2N acetic acid), then 10 cc. of neutral concentrated ammonium-acetate solution. Heat, while stirring, to 60°C., on a water bath and allow to stand. If the precipitate is not too voluminous, it can be filtered on filter paper, otherwise it should be filtered on a gooch with the aid of suction. Wash well with cold water.

The filtrate contains the Be, the precipitate contains the iron and alumina. Add excess NH₃, boil on a hot plate to expel the excess, then filter off the Be(OH)₂ on an ashless filter and wash with hot water containing some ammonium acetate and a few drops of NH₃.

Dry in a platinum crucible, incinerate carefully, and heat in a full Bunsen flame to constant weight. The residue is Be. $\text{BeO} \times 0.3626 = \text{Be}$.

The iron and aluminum can be determined in the hydroquinoline precipitate after destroying the organic matter by a treatment with nitric acid and sulphuric acid.

CHAPTER III

THE ALKALI AND ALKALINE-EARTH METALS

By A. C. LOONAM¹

This chapter deals with eight metals which occupy a peculiar place in metallurgy. Three of them, calcium, sodium, and potassium, are among the five most abundant metals in the earth's crust. Two others, barium and strontium, are plentiful and even the rarest, cesium, is no rarer than such well-known metals as cadmium, mercury, and antimony. Lithium is actually as abundant as zinc, and rubidium is also widely distributed. Their compounds are of great importance in every phase of life, yet the metals themselves are not generally known. Only one of them, sodium, is produced in considerable quantity, but practically all of it goes for use as an industrial chemical and not as a metal.

The reason for this, of course, is that these metals lack the physical properties that make others valuable. They are soft, weak, and rapidly corroded, and are therefore unsuitable for structural purposes. However, they have properties that make them of interest to metallurgists. They are all good conductors of heat and electricity; they form alloys that are liquid at the melting point of ice; their very reactivity makes them valuable as scavengers; their ability to form high melting compounds with some metals has resulted in new methods of metal purification; some of them show definite promise as minor alloy constituents; and last, but by no means least, three of them are becoming very important in the new and rapidly growing field of electronics.

THE ALKALI METALS

The alkali metals, in the order of their economic importance as metals, are sodium, potassium, lithium, cesium, and rubidium. These metals are the most electropositive of all the elements. They are silvery white, soft, and malleable. The hardness decreases in the order Li, Na, K, Rb, Cs. Lithium, the hardest, is softer than lead, while sodium and potassium are readily kneaded in the fingers. All have the same crystal structure, a body-centered cubic lattice.

They are only slightly affected by dry air, but in moist air they quickly become coated with layers of hydroxide and carbonate which are not protective. In the case of lithium, the nitride appears to form first and then is hydrolyzed by the atmospheric moisture. For this reason, they must be kept either in sealed containers or under an inert liquid such as kerosene. When heated in air, they react to form peroxides such as Na₂O₂ and K₂O₄. Lithium is an exception to this in that it forms a mixture of oxide and nitride.

They react vigorously with water, alcohol, and dilute acids at ordinary temperature, with the evolution of hydrogen to produce either the hydroxides or the corresponding salts. These hydroxides are very soluble, strongly alkaline, and very caustic, and are the most stable known in that they can be heated to very high temperatures without dissociation.

The salts of these metals are colorless, except when the acid radical is colored. Most of them are readily soluble in water. The few notable exceptions are the carbonate, phosphate, and fluoride of lithium; the pyroantimonate and some complex

¹ Consulting metallurgist, Deutsch & Loonam, New York.

uranyl acetates of sodium; the chlorplatينات, acid tartrates, hexanitrocobaltates (cobaltinitrites), and perchlorates of potassium, rubidium, and cesium; and the fluosilicates of all the metals except lithium. Cesium also forms insoluble complex chlorides with stannic, plumbic, and antimonious chlorides which are useful in separating it from the other elements. The aluminum alums of potassium, rubidium, and cesium decrease in solubility in the order named and have also been used for separations.

Two unusual properties of these metals are their ability to form salts with hydrogen (hydrides) and their solubility in liquid ammonia. In the hydrides, of the type LiH, the hydrogen is present as a negative ion, just as the chlorine is in NaCl. When fused and electrolyzed, the hydrogen is evolved at the anode. These substances are decomposed by water, liberating one molecule of hydrogen for each molecule of hydride.

Dilute solutions of these metals in liquid ammonia are blue, transparent, and conduct an electric current electrolytically just as do aqueous salt solutions. Concentrated solutions, on the other hand, have a metallic luster and conduct the current electronically as do the metals.

Most of the salts of these elements impart characteristic colors to the Bunsen flame.

The principal physical properties of these metals are given in Table 1.

TABLE 1.—PHYSICAL PROPERTIES

	Li	Na	K	Rb	Cs
Atomic weight.....	6.94	23.00	39.10	85.48	132.91
Specific gravity, 20°C.....	0.53	0.97	0.86	1.53	1.9
Coefficient of expansion per °C. at room temperature, $\times 10^{-6}$	56	71	83	90	97
Melting point, °C.....	186	97.7	63.5	39	28
Boiling point, °C.....	1372	892	774	679	690
Heat of fusion, cal. per g.....	159	27.4	14.7	6.1	3.8
Heat of vaporization, cal. per g.....	4650	1005	484	212	123
Mean specific heat solid, 0° to melting point, cal. per g.....	1.046	0.293	.177	0.083	0.054
Liquid.....	1.08	0.326	.197	0.092	0.060
Gas.....	0.716	0.216	.127	0.058	0.037
Electrical resistivity, μ °C.....	8.55	4.2	6.15	12.5 ^c	18.83
Thermal conductivity, c.g.s. units ^b	0.17	0.323	.237		

^a Microhms per cm. cube.

^b Cal. per sq. cm. per sec. per cm. per °C.

^c 20°C.

SODIUM

Sodium is by far the most important, industrially, of all the metals considered in this chapter.

Occurrence.—Sodium is very plentiful. According to F. W. Clarke it is the sixth most abundant element, making up 2.75 per cent of the 10-mile crust of the earth, or lithosphere, and 1.14 per cent of the watery layer, or hydrosphere. It is an important constituent of the rock-forming silicates.

The most important source of sodium and its compounds is common salt, NaCl, the mineral halite. Enormous deposits of this substance occur in different parts of

the world, the most important United States deposits being in the New York-Pennsylvania-Ohio area, in Michigan, along the Gulf Coast of Mississippi, Louisiana, and Texas, in Kansas, and in the western Virginia-West Virginia area.

While some salt is mined by underground methods, the greater part is recovered by drilling wells, admitting water, and pumping the brine out. Considerable quantities of salt are also recovered from sea water by solar evaporation, from salt lakes, and from underground brines.

Other sodium salts, such as the nitrate, sulphate, carbonates, and borate, are also found naturally in economic quantities. Of these, the nitrate and borate are valuable for their acid radicals, while the output of the others is small compared with supplies from other sources.

Metallurgy. 1. *Thermal.*—Although sodium was first prepared by electrolysis by Davy in 1807, this method was to wait for over three-quarters of a century before being placed in commercial use, mainly because of the lack of large supplies of electric current.

Meanwhile, thermal methods were developed. In 1808, Gay-Lussac and Thenard observed that metallic iron would reduce sodium hydroxide at high temperature. In the same year, Curadon discovered that sodium carbonate could be reduced by charcoal. This process was brought to its highest state of development by H. Sainte-Claire Deville who used the metal in his process for producing aluminum. He heated an intimate mixture of Na₂CO₃, charcoal, and chalk in a horizontal iron retort and condensed the volatilized sodium in a specially designed condenser. This condenser, developed by Donny and Maresca in 1852, presented a large surface for radiation and was a considerable advance over those previously in use. The purpose of the chalk was to prevent the separation of the fused carbonate from the rest of the charge. Later it was found that the addition of iron or its oxide to the charge accelerated the reaction.

Later, H. Y. Castner invented a process in which sodium hydroxide was reduced in iron retorts by highly carburized iron. This apparently was considered an improvement over the Deville process.

Sodium can be liberated from its compounds by other reducing agents. Aluminum, magnesium, and, probably, also calcium and calcium carbide will reduce the hydroxide at high temperatures. Calcium and calcium carbide will react with the chloride. Finally, 75 per cent ferrosilicon will reduce the oxide. This fact has become widely known in the last few years as a result of the use of this reducing agent for the production of magnesium. The sodium present in the calcined dolomite was reduced and volatilized. It condensed at a point nearer the end of the retorts than the magnesium and frequently ignited when the retorts were opened. An outstanding contribution of Dr. L. M. Pidgeon to the success of this process was his development of a condenser in which the sodium was collected separately from the magnesium and therefore had less chance of igniting the latter when it caught fire.

2. *Electrolytic Methods.*—It has not yet been found possible to deposit sodium directly from aqueous solutions of its compounds. The reason for this is the high discharge potential of the metal compared with that of hydrogen. Theoretically, this difference could be overcome by using a solution in which the ratio of concentration of sodium ion to hydrogen ion is sufficiently high or if a high hydrogen overvoltage could be secured at a sodium surface. However, even a saturated sodium hydroxide solution does not give the ion ratio required, and the greatest practical current densities do not give the needed overvoltage.

Sodium can be readily electrolyzed into mercury from aqueous sodium-salt solutions. This is comparatively easy for two reasons: (1) the discharge potential of the sodium is lower because a dilute solution of the metal in mercury is produced,

Neg
ion

Na
Hg

and not the pure metal, and (2) the hydrogen overvoltage at a mercury surface is high. Thousands of tons of sodium are electrolyzed into mercury from NaCl solutions in alkali-chlorine cells every year only to have the amalgam decomposed by reaction with water to produce caustic soda.

The possibility of recovering the sodium by distillation of the mercury from this amalgam has attracted the attention of inventors for many years, and this interest continues. The chief difficulties apparently have been the large amount of mercury to be distilled per unit of sodium produced, losses of mercury in the process, and the difficulty of removing the last traces of mercury from the sodium. However, the application of modern physicochemical methods may overcome these and make the process commercially feasible. One recent patent,¹ for instance, calls for cooling of the amalgam from the cell to crystallize out a solid phase much richer in sodium, which is removed by filtration and treated further while the impoverished mercury is returned to the cell. Another² describes the use of an alkaline-earth metal, such as calcium, to remove the last traces of mercury from the molten alkali metal in a manner similar to the use of zinc in the Parkes process.

At the present time, practically all metallic sodium is produced by the electrolysis of fused salts. A great many ingenious cells have been designed for this purpose, some of them even reaching the stage of commercial operation, but only two, those of Castner and of Downs, have stood the test of time.

The Castner Cell.—The development of direct-current generating machinery during the seventies and eighties of the last century provided the large supplies of cheap electric power required for electrolytic processes. H. Y. Castner patented his cell in 1890. It quickly displaced the thermal processes and reached a dominant position, which it held until about 1924 when the Downs cell appeared. It is now no longer in use in the United States.

The cell, which is shown in Fig. 1, consisted of a cast-iron pot open at the top and with an opening at the bottom to which an iron sleeve was attached. The iron cathode leadin passed up through this sleeve and was held in place and insulated from it by frozen electrolyte. The cathode itself, the enlarged end at the top of the leadin, was also of iron. The anodes were suspended from the cover of the cell, to which the positive lead was attached, and were of iron or nickel; if of iron, the anode and cover were sometimes cast in one piece. Through a hole in the center of the cover, and carefully insulated from it, was suspended another iron sleeve to the bottom of which was attached a cylinder of iron or nickel gauze. This cylinder served as a metal well and had a removable cover to permit removal of metal, while the gauze that hung between the electrodes prevented the sodium from reaching the anode, since its high surface tension and its inability to wet the gauze prevented it from passing through the meshes. The cell cover had openings for feed and for escape of gases.

The electrolyte was fused sodium hydroxide. This material has several advantages: its melting point is low, 318°C., it is not corrosive to iron, and the anode product, oxygen, permits the use of iron or nickel as anode, and requires no elaborate collecting system.

The temperature of operation was kept as low as possible, not more than 10 to 20° above the melting point of the bath, which was lower than that of pure caustic because of the presence of impurities, including water. The reason for this was that the current efficiency fell off rapidly and became small at only slightly higher temperatures. Even at best, the efficiency could have been no better than 50 per cent, as an amount of hydrogen equivalent to that of the sodium was liberated at the cathode. This hydrogen came from decomposition of the water which was produced together

¹ U. S. patent 2224814.

² British patent 505112, May 4, 1939.

with oxygen by the discharge of OH⁻ ion at the anode and carried to the cathode. The solubility of water in NaOH at operating temperatures is considerable. The presence of this hydrogen necessitated the greatest care to prevent its mixing with oxygen and causing explosions. As it was, minor explosions were of frequent occurrence owing to a number of reasons.¹

During operation the liberated sodium was removed from the metal well by means of a perforated ladle which permitted the fused bath to drain off while retaining the metal. In actual practice, the current efficiency averaged about 40 per cent, while the cell voltage was about 5.0. The energy consumption was therefore about 6.6 kw-hr. per lb. of metal.

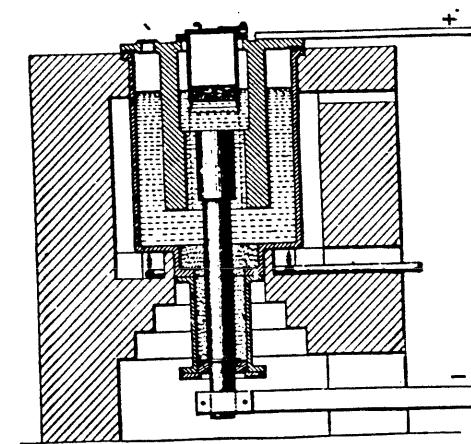


FIG. 1.—Castner cell.

The Downs Cell.—The logical raw material for the production of metallic sodium is common salt. It is cheap and plentiful, chlorine can be recovered as a coproduct, and current efficiencies much greater than 50 per cent should be obtainable. On the other hand, it has a number of disadvantages; its melting point is high (803°C.), a temperature at which the vapor pressure of sodium, which is lighter than salt, is almost half an atmosphere; it rapidly attacks refractories; and the chlorine produced is difficult to handle. Its advantages were early recognized, and numerous attempts were made to overcome the difficulties. Some workers, such as Ashcroft and Carrier, tried to use a divided cell similar to the mercury caustic-chlorine cell. Molten salt was electrolyzed in one compartment with a graphite anode and a molten lead cathode. The chlorine given off at the anode was collected, while the lead-sodium alloy was caused to flow to another compartment containing molten caustic soda. Here it served as an anode with the result that the sodium was electrolyzed out of the alloy and deposited on an iron cathode suspended in the bath. Other workers, including McNitt and Seward and von Kugelgen, attempted to produce the sodium directly.

It remained, however, for J. C. Downs,² in 1924, to solve all the difficulties involved. This cell, which is shown in Fig. 2, and which now accounts for by far the greater part of the sodium produced in the United States, must be ranked with the Hall aluminum cell and the Dow magnesium cell as one of the most successful fused electrolytic cells yet developed. It consists of a steel box lined with refractory and insulating brick. The graphite anode extends downward through the bottom of the

¹ ALLMAND and ELLINGHAM, "Applied Electrochemistry," p. 498.

² U. S. patent 1501756 (1924).

tank to the electrical connections. The cathode is an iron ring supported on iron leads that extend through the sides of the cell to the electrical connections. Over the anode, and submerged in the electrolyte, is a conical bell which, according to the patent, may be of iron or refractory, for collecting the chlorine. Surrounding the lower edge of the bell is an inverted annular launder, also submerged, for collecting the sodium. Screens attached to the edges of this launder and extending downward on both sides of the cathode serve to prevent the sodium from being carried away. A riser attached to the top of the launder permits the metal to flow continuously into an external sump. The riser extends far enough above the bath level so that the metal, because of its low specific gravity, can overflow but the bath cannot. The riser and sump also permit the metal to cool before it is discharged. An opening in the cell cover is provided for charging.

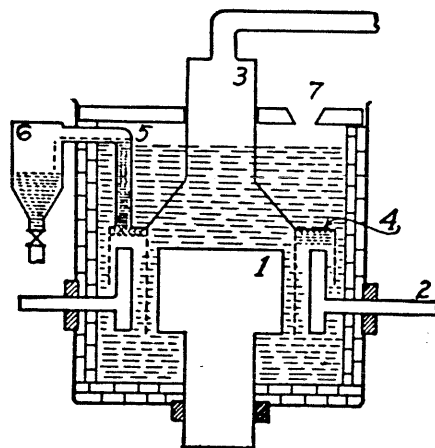


FIG. 2.—The Downs sodium cell. (From Riegel's "Industrial Chemistry," p. 314, courtesy of Reinhold Publishing Co.)

The electrolyte is not pure salt but a mixture of this with calcium chloride. These form a eutectic containing 66.8 per cent CaCl_2 and melting at 505°C . The use of this mixture, with its lower melting point, permits lower operating temperatures with resulting reduced wear and tear on the cell parts. The actual operating temperature is around 600°C .

The metal deposited at the cathode is not pure sodium but an alloy containing calcium. The amount of calcium in the alloy is not known, but calculations based on the Ca-Na equilibrium diagram and thermodynamic data indicate a concentration of 1.4 per cent if the bath has the eutectic composition. It may be higher than this but cannot exceed about 5.5 per cent, the solubility limit at 600° .

It can be removed by cooling as its solubility decreases rapidly as the temperature is reduced, becoming about 4 per cent at 400° , 2 per cent at 200° , and a very low value at the melting point of sodium, 97.7°C . If the cooling in the riser is considerable, an appreciable amount may crystallize out there and, because of its higher density, fall back into contact with the electrolyte and react with it to reproduce the equilibrium alloy. Other methods can also be used. R. E. Hulse has patented¹ a method in which the calcium containing alloy is brought into contact with solid salt, whereupon the calcium forms calcium chloride and sodium. Finally, the method, mentioned above, of using calcium to remove mercury from sodium can probably be turned

¹ U. S. patent 2224820.

around; *i.e.*, mercury can be used to remove calcium. In any case, the purity of the metal marketed leaves little to be desired as it is considerably better than 99.9 per cent.

The chlorine produced by the cell is pure enough to be liquefied.

The salt is very carefully purified and heated to a high temperature to remove all possible water before being fed to the cell. In spite of this, some water gets in and causes minor explosions during operation.

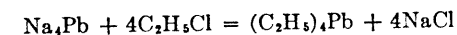
The current efficiency of the cell is high, probably better than 85 per cent. Mantell² gives the voltage as about 7. These correspond to an energy consumption of 4.4 kw.-hr. per lb. of metal.

The sodium is cast into 1-, $2\frac{1}{2}$ -, and 12-lb. ingots or "bricks" which are packed in removable head drums holding 280 lb. or in cases of 50 and 100 lb. Larger quantities are shipped in tank cars similar to those used for sulphuric acid and other industrial chemicals. The cars, made by the American Car & Foundry Co., and possibly by other manufacturers, hold 40 tons each. The molten metal is pumped into them, allowed to freeze, and remelted before unloading. This is probably the only case in which a metal has been shipped in such a manner. The low melting point, low specific gravity, and fairly large-scale production and use make this possible.

Production and Prices.—According to T. P. Hou,² there were two plants producing sodium in the United States, one at Niagara Falls, N. Y., and the other at Baton Rouge, La., with a total capacity of 120 tons a day as of the end of 1940. The world production for 1941 was estimated at 300,000 tons.³

The present published price is $15\frac{1}{2}$ cents per lb., f.o.b. Niagara Falls, for untrimmed bricks.

Uses.—The present important uses for sodium are based entirely on its chemical properties. Large quantities are made into a lead-sodium alloy for the manufacture of tetraethyl lead for high-octane gasoline. The alloy reacts with ethyl chloride in accordance with the equation



An important product, from a metallurgical standpoint, is sodium cyanide. When the metal is heated in ammonia, it forms sodamide, and this, when treated with charcoal, yields sodium cyanide. This high-grade product is used in electroplating and in heat-treatment of metals. CA

When heated in excess air or oxygen, sodium does not form the normal oxide but goes over to the peroxide, Na_2O_2 , a light yellowish-white powder. This substance is really a salt of hydrogen peroxide and is therefore a powerful oxidizing agent. It is manufactured on a large scale and is widely used as a bleaching agent and for the manufacture of other oxidizing agents such as sodium perborate.

Sodium is also an essential raw material in the manufacture of a number of important organic compounds.

Of interest to metallurgists is the fact that a small amount of sodium (0.05 per cent) added to aluminum-silicon casting alloys shifts the eutectic composition from the normal value of 11.7 per cent silicon to 14 per cent. The eutectic temperature is also lowered from 577 to 564°C . By this treatment the microstructure of an alloy with 13 per cent Si, which would normally contain brittle primary crystals of silicon in a ground mass of Al-Si eutectic, is transformed into one with primary crystals of aluminum in a ground mass of extremely fine eutectic with a resultant improvement in physical properties, notably in tensile strength and elongation. According to

¹ "Industrial Electrochemistry."

² "Manufacture of Soda," 2d ed., p. 329.

³ *Mineral Ind.*, Vol. 50, p. 611.

Edwards, Frary, and Jeffries,¹ the optimum concentration of sodium in the alloy is 0.014 per cent, but an excess must be added to allow for losses.

Sodium is an excellent conductor of electricity. On a volume basis its conductivity is about 36 per cent of that of copper, but on a weight basis it is about 3.3 times as good. Some years ago the Dow Chemical Co. built an outdoor conductor of sodium-filled steel pipe, with a capacity of 4000 amp. direct current. An article² was published describing the installation, and it was stated that no appreciable increase in resistance was noted after 10 months' service.

Addition of sodium to the mercury used in the amalgamation of gold ores sometimes improves recovery. This was also recommended at one time for platinum ores. The sodium increases the ability of the mercury to wet the precious metals. This same property is the basis of a recommendation that small amounts of sodium be added to metals used for hot-dip coatings.

The metal has been recommended as a heat-transfer medium because of its low melting point, high boiling point, and excellent thermal conductivity. It is completely inert in iron and steel in the absence of air and moisture. An interesting use in this connection is in airplane-engine valves. These are made hollow and are partially filled with sodium, which aids in keeping them cool by greatly increasing the heat transfer from the head to the stem and thus to the lubricant.

Another use for the metal is the removal of arsenic and antimony from lead-tin alloys. However, anyone using this process should remember that the dross formed will contain sodium arsenide which reacts readily with moisture, even that in the air, to form arsine, an extremely poisonous gas.

A very important application, although it accounts for only a small consumption of the metal, is the sodium-vapor lamp now widely used for highway lighting. In this lamp an electric current is passed through sodium vapor at low pressure, causing it to emit the well-known D lines of the sodium spectrum. These lines account for a large fraction of the energy supplied and lie in the region of the spectrum to which the human eye is most sensitive. The lamp is therefore very efficient.

POTASSIUM

This metal is much less important commercially than sodium.

Occurrence.—Potassium is the seventh most abundant element in the earth's crust according to F. W. Clarke, who states that it accounts for 2.58 per cent of the lithosphere and 0.04 per cent of the hydrosphere. These figures show an important difference between this metal and sodium in that, although it is almost as abundant in the solid crust of the earth as the other, it is much less so in the waters, principally, of course, the oceans. This tendency of potassium to remain in or return to the solid phase has the important consequence that large deposits of soluble salts of this metal occur much less frequently than those of sodium. However, rare though they are, they are the chief commercial sources of the metal and its compounds.

The principal deposits of potassium salts are at Stassfurt, Germany, in Alsace, France, and in the area around Carlsbad, New Mexico. Other sources that have produced commercial quantities are the nitrate beds in Chile which contain appreciable quantities and from which a nitrate high in potassium has been produced, underground brines at Salduro, Utah, Searles Lake in California, and the Dead Sea in Palestine, the waters of which are high in potassium salts and constitute the richest source in the British Empire. During the First World War considerable quantities were recovered from cement plants. The potassium in the rock was volatilized in the kilns and recovered in Cottrell precipitators.

¹ "The Aluminum Industry," Vol. II, pp. 72-75, 209-215.

² *Trans. Electrochem. Soc.*, Vol. 62, p. 151, 1932.

The discovery of the Carlsbad deposits during the 1920's was of extreme importance to the United States. It provided this country with its own supply of this important fertilizer and avoided the situation that occurred during the First World War when our supply from Germany was cut off.

In the Stassfurt deposits, the potassium occurs as a number of complex salts from which it is recovered by leaching and fractional crystallization. The working out of this process represents one of the first and one of the greatest triumphs of modern physical chemistry and the application of the phase rule.

The Carlsbad deposits consist mainly of a mixture of sylvite, KCl, and halite, NaCl, although one mine contains a commercial deposit of langbeinite, $K_2SO_4 \cdot 2MgSO_4$. The two chlorides are separated by flotation in saturated brine. There are two processes in use; in one the halite is floated away from the sylvite, while in the other it is the sylvite that floats.

Metallurgy. 1. *Thermal.*—Potassium can be prepared by any of the methods used for sodium. Reduction by carbon, however, is complicated by the fact that, unlike sodium, metallic potassium tends to combine with carbon monoxide to form a highly explosive compound of the formula $K_2C_2O_2$. The metal vapor must be condensed and the liquid metal cooled rapidly to a low temperature to avoid its formation. Rubidium and cesium act similarly to potassium.

The dolomite supply of one of the magnesium plants using the Pidgeon process during the Second World War contained potassium as well as sodium. Both were reduced by the ferrosilicon with the result that a liquid Na-K alloy was condensed which could be tapped from the retorts by opening a valve. Consideration was given to recovering the potassium from this alloy by fractional distillation but, so far as is known, no actual production came from this source.

The principal producer of sodium for general industrial use in the United States is making a commercial grade of potassium by treating one of its salts, presumably the chloride, with sodium. It would be difficult and expensive to prepare metal substantially free from sodium by this process, but the crude product should be entirely suitable for most commercial purposes.

2. *Electrolytic.*—As in the case of sodium, potassium has not yet been deposited directly from aqueous solutions, but; also similarly to sodium, it can be electrolyzed into a mercury cathode. This could be the basis of a process for the recovery of this metal just as for the other but, judging from the patent literature, the interest has been much less than in the commercially more important sodium.

The metal can be produced by electrolysis of its fused hydroxide. The Castner sodium cell, however, is not suitable for this purpose as it does not provide sufficient protection of the metal from the air since potassium is much more reactive with oxygen than sodium. On the other hand, as von Hevesy¹ showed, if suitable precautions are taken, higher current efficiencies can be secured with this metal than with the other, as its solubility in its hydroxide is less and its rate of diffusion lower. He used a cathode surrounded by a magnesia crucible to protect the metal from the air. O. P. Watts² describes a laboratory experiment for making potassium which is based on von Hevesy's work. He recommends thrusting an iron wire cathode through the bottom of a magnesium oxide crucible and inverting this in the fused KOH. A piece of sheet iron is used as an anode. There are explosions when the current is first turned on owing to reaction of the potassium with the air in the crucible. The author states that a current efficiency of about 58 per cent has been obtained with this arrangement.

¹ *Z. Elektrochem.*, Vol. 15, p. 539, 1909.

² "A Laboratory Course in Electrochemistry."

Na
Au
Pt
Hg-Na

Removal
of
As & Sb
arsine

Explosive

The production of potassium by electrolysis of its fused chloride presents a number of difficulties, one of which is the fact that its boiling point is about the same as the melting point of the chloride (774°C.). Because of the strongly electropositive nature of the metal, there are relatively few salts that could be added to the bath to reduce its melting point without fear of contamination. Potassium fluoride, which forms a eutectic with the chloride having a melting point of 605°C., appears to be the most promising, with barium chloride (melting point of eutectic 660°) a possibility and potassium bromide suitable for laboratory work. A. Matthiessen claimed, in 1855, that he obtained potassium free from calcium by electrolyzing an "equimolecular" mixture of potassium and calcium chlorides, but there is some reason to doubt this. Although his mixture probably contained 66 $\frac{2}{3}$ molecular per cent KCl (calcium was considered to have a valence of one at that time), Moldenhauer and Anderson¹ recovered a product that was chiefly calcium from a bath containing 69 molecular per cent KCl, although there was evidence that some potassium was formed.

Linneman produced the metal by the electrolysis of fused potassium cyanide.

Production, Prices, and Use.—There is no information available regarding production and prices. The metal has no large-scale application. Its high equivalent weight and high price compared with sodium discourage its use even where its greater reactivity would cause it to be preferred. Increased availability may, however, change this situation.

One important use, which, however, accounts for only a minor consumption, is that in photoelectric cells. The photosensitivity of potassium extends into the visible region of the spectrum and is superior to that of sodium in this respect and, although inferior to cesium and rubidium, the metal is much more plentiful.

Sodium and potassium form alloys that are liquid at ordinary temperatures. That with the lowest melting point, -12.5°C., has the composition 22.7 per cent sodium and 77.3 per cent potassium. These alloys have been suggested for use in high-temperature thermometers.

LITHIUM

Lithium is the lightest of all the metals. Although it is definitely a member of the alkali group, it resembles the alkaline earths in some of its properties, such as the low solubilities of its carbonate, fluoride, and phosphate and its formation of a stable carbide and silicide.

Occurrence.—Although generally considered a rare element, lithium is really as abundant in the earth's crust as zinc and more so than such common metals as lead, tin, cadmium, and antimony. However, it is widely distributed, and there are comparatively few workable deposits.

Spodumene, LiAl(SiO₃)₂, and the lithia micas, lepidolite and zinnwaldite, are economically the most important lithium minerals. Spodumene, which contains about 3 to 8 per cent Li₂O, is the chief source in the United States. It is mined in South Dakota and in North Carolina near Kings Mountain. In both localities, it occurs associated with other minerals and is recovered by flotation. According to Bowles,² mill capacity for spodumene concentrate was 2000 tons a month at the end of 1943. Another important source is Scarles Lake brine from which lithium sodium phosphate is recovered. About 300 tons of this material was shipped in 1938. Some lepidolite is also produced in the United States, but most of this goes directly into glass and ceramic manufacture, very little being used for the production of lithium salts.

¹ *Z. Elektrochem.*, Vol. 19, p. 444, 1913.

² *Mining Met.*, Vol. 25, p. 85, 1944.

Lithium is extracted from silicate minerals by heating a mixture of the finely powdered material with an excess of potassium sulphate to a moderate red heat, care being taken to keep the temperature below the melting point of any of the constituents of the mixture.¹ An exchange reaction takes place, the potassium replacing the lithium which is converted to a soluble sulphate. The cooled mass is leached with water and the lithium precipitated from the solution as the carbonate, from which other salts can be made.

F. Fraas and O. C. Ralston, at the U. S. Bureau of Mines, recently worked out a process² in which spodumene is mixed with calcium chloride and lime and heated in a rotary kiln. The lithium is volatilized as chloride and is collected in scrubbers and Cottrell precipitators. No information is available as to whether this process has yet been applied commercially.

Metallurgy. 1. *Thermal.*—Unlike the other alkali metals, lithium oxide or carbonate cannot be reduced to metal by carbon since a stable carbide is formed. Mellor³ states that metallic calcium will reduce the chloride but that the resulting alloy contains 3 to 4 per cent calcium which is difficult to separate. He also states that the hydroxide cannot be reduced by magnesium because the reaction proceeds with explosive violence. This is to be doubted. Hackspill and Pinck⁴ found that magnesium, aluminum, and iron reduce lithium oxide in high vacuum. The reaction with magnesium takes place at 450°, with aluminum at 1150°, while that with iron is incomplete at 1300°.

Thermal processes have so far not been important in the metallurgy of lithium. Unlike sodium and potassium, commercial production developed after the introduction of the electric generator.

2. *Electrolytic.*—Like sodium and potassium, lithium has not been deposited directly from aqueous solutions. However, as in the case of the other two, amalgams can be prepared.

At the present time, the metal is produced commercially by the electrolysis of its fused chloride. According to Osborg (*op. cit.*), the pure chloride is unsuitable even though it has a comparatively low melting point, 610°. The voltage soon rises and electrolysis ceases. However, the addition of KCl overcomes these difficulties, and this bath operates continuously in large units and at high yields. Current efficiency is high, over 90 per cent, and the lithium recovery, based on LiCl fed, is over 95 per cent.

To ensure pure metal, the chloride must be pure, the cells constructed of materials that are not attacked by the highly corrosive bath, and the metal itself protected from the nitrogen of the air with which it readily combines. As a result of controlling these factors, the purity of the metal has reached 99.5 per cent with a nitrogen content of 0.03 per cent. The lithium chloride should be free from water before it is added to the cell. Izgaruishev and Pletnev⁵ as a result of work with a 225-amp. cell recommend a 1:1 mixture of LiCl and KCl as electrolyte with iron cathodes and graphite anodes. They give the cell voltage as 17, current efficiency as 85 per cent, and the direct-current power consumption as 34 kw.-hr. per lb. (75 kw.-hr. per kg.). The voltage appears to be much too high.

An interesting method of preparing lithium is due to L. Kahlenberg.⁶ He electrolyzed a concentrated solution of LiCl in pyridine. Using a carbon anode and a bright iron cathode, and a current density of 0.2 to 0.3 amp. per sq. cm. (1.9 to 2.8 amp. per sq. ft.), he secured a dense, silver white, adherent deposit of metallic lithium.

¹ OSBORG, monograph "Lithium," Electrochemical Society, 1935.

² *Bur. Mines Rept. Investigations* 3344.

³ "Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. 2, p. 450.

⁴ *Bull. soc. chim. France*, Vol. 49, pp. 54-70, 1931.

⁵ *Izvestnie Metal*, p. 536, 1932.

⁶ *Jour. Phys. Chem.*, Vol. 3, p. 601, 1899.

The potential drop across the cell was 14 volts. Lithium chloride is very soluble in a number of organic solvents.

Production, Prices, and Uses.—No published information as to production has been found since 1929, when it was stated¹ that the United States production was 100 lb. per day. It has probably increased since that time. According to recent quotations, the price for 98 to 99 per cent metal is \$15 per lb. in 100-lb. lots.

Osborg (*op. cit.*) lists a large number of possible uses for lithium. Among these are the preparation of oxygen-free copper of high electrical conductivity and the degassing and purification of copper and copper-base alloy castings. Master alloys are commercially available for greater convenience in adding the lithium. Other suggested uses are the treatment of iron and stainless steel and as an alloying constituent with aluminum, lead, magnesium, and zinc. Some years ago, a lead-base bearing alloy was developed in Germany and found extensive use. Called "B-Metal" it contained approximately 0.04 per cent Li, 0.66 Na, 0.73 Ca, 0.03 K, less than 0.2 per cent Al, balance lead. An aluminum-base alloy, Scleron, which contained lithium, was also placed on the market in Germany for structural uses. Its composition was 83 Al, 12 Zn, 2 Cu, 0.5 to 1 Mn, 0.5 Fe, 0.5 Si, 0.1 Li.

An interesting compound of lithium, prepared by heating the metal in hydrogen, is the hydride, LiH, to which reference was made in the introduction to this section. It is a solid with a melting point of 680° and reacts with water to liberate hydrogen. It has been proposed as a means of transporting this gas, as 1 lb., reacting with water, yields about 45 cu. ft., at ordinary temperature and pressure. It also reacts readily with other substances.

The metal also has possible applications in organic chemistry.

A recently announced metallurgical use for lithium compounds is their addition to the atmospheres of steel heat-treating furnaces. It is claimed that their presence prevents scaling and decarburization of the steel during treatment.

CESIUM

Cesium is the most electropositive and the most reactive at ordinary temperatures of all the metals.

Occurrence.—Cesium is the rarest of all the elements considered in this chapter. It is present in the earth's crust to the extent of about 0.000008 per cent, approximately the same as cadmium, mercury, and iodine. It is widely distributed and occurs in some mineral springs and in minute amounts in sea water.

The principal mineral source is pollucite, $H_2Cs_4Al_4(SiO_3)_8$, the only cesium mineral known. It occurs on the island of Elba, where it was first discovered.

For a time the only commercial deposit in the United States was in Maine, but in 1938, an important strike at the Tin Mountain mine in South Dakota was announced.² By the end of that year, over 100,000 lb. of ore containing 1 to 30 per cent Cs_2O had been produced.

Cesium can be extracted from the finely ground mineral by digestion with strong hydrochloric acid. The resultant solution is treated with a solution of antimony trichloride to precipitate the cesium as a complex chloride.

Lepidolite frequently contains significant amounts of cesium which can be recovered as a by-product when the mineral is treated for lithium.

Metallurgy. 1. *Thermal.*—Cesium metal can be produced by reduction of the carbonate with carbon, but like potassium, it forms an explosive compound with carbon monoxide. It can also be prepared by reduction of the chloride with calcium or calcium carbide or of the hydroxide with aluminum or magnesium. In all these pro-

¹ *Mining Met.*, Vol. 11, p. 47, 1930.

² *Mining Met.*, Vol. 20, p. 9, 1939.

cesses the metal is liberated as vapor and condensed. Reduction of the chloride by calcium, which has been described by Hackspill,³ appears to be the simplest process as no gas is evolved and the entire operation can be conducted in a vacuum. Polyakov and Fedorov⁴ tried calcium carbide instead of the metal and obtained 75 per cent recovery of the cesium as metal. However, the reduction of the hydroxide by magnesium, investigated and fully described by Erdmann and Menke⁵ and by Richards and Brink,⁶ appears to be equally efficient provided certain precautions are observed. The reaction is carried out at a red heat in an iron tube through which a current of dry hydrogen is passed, and care must be taken to avoid too rapid heating and to maintain a flow of hydrogen.

Hackspill and Pinck⁵ found that the sulphate, arsenate, thiocyanate, and other salts could be reduced by iron in a vacuum. The sulphate and arsenate were reduced at their melting points, the thiocyanate at 650°, while the borate and phosphate required temperatures of 1300 to 1400°C.

2. *Electrolytic.*—As in the case of potassium, cesium amalgam can be prepared from aqueous salt solutions, but the metal itself has not been deposited. It has been prepared by electrolysis of a fused mixture of cesium and barium cyanides.

Production, Prices, and Uses.—There is no available information as to production and prices. However, the total United States production of the metal and its salts probably does not exceed 500 lb. per year. Small though this is, it is very important because of the uses of the metal in electronics. Cesium is the only metal that gives off electrons when it is exposed to visible light of all colors. It is therefore widely used in photoelectric cells. Furthermore, by depositing exceedingly thin layers of cesium and oxygen on silver, a surface is obtained that is not only much more sensitive than one of pure cesium, but its sensitivity extends far into the infrared region of the spectrum. Because of these properties, this surface is used in the modern television camera and in "black light" signaling devices.

Another valuable property of the cesium-oxygen-silver surface is its efficiency as a secondary electron emitter. When struck by an electron, it gives off as many as nine secondary electrons, and it is therefore used in an extraordinary amplifying device called the "electron multiplier." Amplifications of as high as 5 million have been obtained in 10 stages with this instrument.

RUBIDIUM

Rubidium is the least important, economically, of the alkali metals.

Occurrence.—Rubidium is about ten times as abundant as cesium, but up to the present, no mineral of which it is a major constituent has been found. It has been found in sea water, mineral springs, carnallite from the Stassfurt deposits, and in lepidolite. The last is the principal source, but reasonable quantities could be recovered from the Stassfurt mother liquors if a demand were to develop.

Metallurgy.—The methods described for the preparation of metallic cesium apply equally to rubidium with only one possible exception, the electrolysis of the fused cyanide. However, rubidium has been prepared by the electrolysis of its fused hydroxide.

Production, Prices, and Uses.—There is no published information about production or prices. The metal has no use of any importance. It suffers from the fact that most of its properties are intermediate between those of potassium and cesium.

¹ *Compt. rend.*, Vol. 141, p. 106, 1905.

² *Jour. Applied Chem. (U.S.S.R.)*, Vol. 13, p. 1833, 1940.

³ *Jour. Am. Chem. Soc.*, Vol. 21, p. 259, 1899.

⁴ *Ibid.*, Vol. 29, p. 125, 1907.

⁵ *Bull. soc. chim.*, Vol. 49, p. 54, 1931.

THE ALKALINE-EARTH METALS

The alkaline-earth metals, in the order of their economic importance, are calcium, barium, and strontium. Radium also belongs to this group, but it will not be discussed in this chapter as it is important for its radioactive properties and is used only in the form of its salts. (See Chap. XXIII.)

These metals are silvery white, malleable, and comparatively soft, although calcium, probably the hardest, is considerably harder than lead. Although second only to the alkali metals in electropositive character, they differ markedly from them. They have much better physical properties, higher melting and boiling points, and are generally less reactive at ordinary temperatures. Calcium, for instance, is moderately stable in the air, decomposes water only slowly, and is not attacked by alcohol. However, reactivity increases with atomic weight, and barium is about as active as lithium.

Strangely enough these metals are not so easy to produce as those of the alkali group. There are a number of reasons for this, among which are their high melting and boiling points, their great reactivities at high temperatures, and the fact that they form stable carbides, nitrides, and silicides. It is even more difficult to purify them as, in the liquid state, they dissolve not only other metals but also their own nitrides and silicides. Indeed it is only in recent years that even calcium has been prepared reasonably free from nitrogen. As a result only the latest determinations of physical properties are likely to be reliable. The situation is even worse in the cases of strontium and barium.

The salts of these metals, like those of the alkalis, are generally colorless except where the acid radical is colored. On the other hand, many more of them are insoluble or only sparingly soluble. Among the most important compounds in this class are the hydroxides, carbonates, fluorides, sulphates, and silicates. Because of the less

TABLE 2.—PHYSICAL PROPERTIES OF ALKALINE-EARTH METALS

	Ca	Sr	Ba
Atomic weight.....	40.08	87.63	137.36
Specific gravity 20°C.....	1.54	2.6	3.5
Coefficient of expansion per °C. at room temperature, $\times 10^{-6}$	25		
Melting point, °C.....	851	771	704
Boiling point, °C.....	1487	1384	1638
Heat of fusion, cal. per g.....	55.7	25.0	10.2
Heat of vaporization, cal. per g.....	911	383	260
Specific heat, room temp., cal. per g.....	0.157		0.68
Electrical resistivity, ¹ 0°C.....	3.43	22.76 (20°)	
Ultimate tensile strength, lb. per sq. in. ²	6300		
Proportional limit, lb. per sq. in.....	1500		
Elongation, per cent.....	53		
Reduction in area, per cent.....	62		
Hardness, Brinell.....	13		
Modulus of elasticity, lb. per sq. in.....	2,900,000– 3,700,000		

¹ Microhms per centimeter-cube.

² Mechanical properties are from *Nat. Bur. Standards Circ. C 447* and were determined on distilled metal containing 99.3 per cent Ca, 0.14 per cent Si, 0.02 per cent Fe.

electropositive character of these metals, their salts with weak acids are more readily decomposed and those with strong acids show some tendency to hydrolyze in the presence of water. The hydroxide and carbonate of calcium, for instance, are readily converted to the oxide by heating, and it is difficult to prepare anhydrous calcium chloride because of hydrolysis. However, the metals become more electropositive with increasing atomic weight, and barium salts are much more stable. To convert barium carbonate to the oxide, it must be heated with coke to reduce the carbon dioxide, and barium chloride can be readily dehydrated.

These metals form saltlike hydrides and dissolve in liquid ammonia like the alkali metals. Their salts impart characteristic colors to the Bunsen flame.

Physical Properties.—All these metals crystallize in the cubic system at ordinary temperatures, calcium and strontium with face-centered lattices and barium with a body-centered lattice. Calcium and barium show polymorphism. The transition point for calcium is at 450°C., with a possible second one at 300°, while that for barium is at 375°. The high-temperature form of calcium is hexagonal, close packed. So far, no evidence of a transition has been found for strontium. The physical properties of the metals are summarized in Table 2.

CALCIUM

This metal is the most important of its group.

Occurrence.—Calcium is the fifth most abundant element, constituting, according to F. W. Clarke, 3.64 per cent of the earth's crust. The most important source of the metal and its compounds is, of course, calcium carbonate in its various forms, limestone, marble, oyster shells. Large deposits of these materials are found in all parts of the globe. Other calcium minerals occur in economic quantities, but except for calcium fluoride, the mineral fluorite or fluorspar, which is sometimes added to the electrolytic bath, none are important in its metallurgy.

Calcium carbonate, when heated to a high temperature, gives off carbon dioxide and is converted to calcium oxide, quicklime, or simply lime, the most important industrial alkali. Thousands of tons of lime are made daily in rotary kilns and shaft furnaces.

Some 2 to 3 million tons of calcium chloride a year are potentially available in the residual liquors from the ammonia-soda or Solvay process. Some is recovered for a number of uses, but the greater part is run to waste.

The raw materials for calcium production are therefore abundant.

Metallurgy. 1. *Thermal.*—Calcium can be prepared by a number of thermal methods. Moissan made it by heating the anhydrous iodide with sodium to produce a sodium-calcium alloy. Treatment with alcohol dissolved the sodium, leaving calcium of about 99.3 per cent purity.

According to a number of recent patents,¹ calcium can be produced by heating calcium oxide with silicon or aluminum in an evacuated retort in a manner similar to the production of magnesium. As in the other process, the addition of a small amount of a fluoride, 0.5 to 5 per cent, is said to promote the reaction. That calcium can be produced in this way is not surprising, as Gunz and Matignon used it to produce metallic barium over thirty years ago.

A recent United States patent² claims that the reduction with silicon can be carried out in an arc furnace.

The fact that lime can be reduced with silicon probably means that it can also be reduced by calcium silicide, an electric-furnace product, with resulting increased yield,

¹ British patent 497772, Dec. 28, 1938, to Magnesium Elektron, Ltd.; French patent 830187 to I. G. Farben.

² U. S. patent 2225536.

and that the silicide itself will dissociate on heating *in vacuo* to produce calcium and silicon.

As a result of the experience gained with magnesium, these processes may become very important as sources of calcium in the not far distant future. One advantage of calcium over magnesium lies in its higher equivalent weight. 20 lb. of calcium require only as much reducing agent as 12 lb. of magnesium at the same efficiency.

The metal can also be produced by reduction of lime with carbon. This is far more difficult and complicated than in the case of the alkali metals and, so far as is known, has not been worked on a commercial or even on a large pilot-plant basis. The method is a two-stage one. When lime and coke are smelted in an electric furnace, the product is calcium carbide. This is produced on a large scale as a source of acetylene and other products. It has been known for some time that, when heated to a very high temperature, calcium carbide dissociates into graphite and calcium vapor. The vapor pressure of the calcium has been measured. Recently, Manderli, Moser, and Treadwell¹ produced compact calcium by heating the carbide to 1600 to 1800°C. in a vacuum.

Hanawalt, Nelson, and Ward² have patented processes in which calcium carbide is heated with calcium silicide or with metallic iron. The calcium distills off, leaving a residue of silicon carbide or of carburized iron.

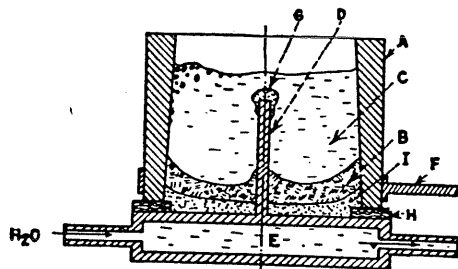


FIG. 3.—Submerged cathode cell.

Calcium carbide is now being used to make calcium-lead alloys. By heating it with lead under a chloride flux, alloys containing 3 to 4 per cent calcium are obtained.

2. *Electrolytic.*—Calcium, like the alkali metals, has not been deposited from aqueous solutions, but, also like them, amalgams can be produced by using a mercury cathode. A crude metal, probably a high-calcium amalgam, has been obtained in this way on a small scale.

Most of the commercial calcium on the market at the present time is produced by the electrolysis of its fused chloride. This is not an easy operation. It is difficult to prepare the anhydrous chloride free from basic salts and oxide, and apparently, it has not yet been found possible to run a calcium cell on hydrated feed as is done with magnesium. Another difficulty is the high melting point of calcium (851°C.). Although this is reduced to the neighborhood of 800°C. by impurities, the bath would have to be operated at about 900° if liquid metal were to be tapped off, a temperature at which the metal reacts vigorously with air to form oxide and nitride which rapidly thicken the bath and render it useless. Furthermore, at this temperature, the metal rapidly diffuses through the bath, becomes chlorinated at the anode as rapidly as it is deposited at the cathode, and electrolysis soon stops. Attempts to operate below the melting point of the metal yield only a voluminous sponge, which grows rapidly to the anode and is so full of electrolyte that it is of little or no value.

¹ *Helvetica Chim. Acta*, Vol. 27, p. 105, 1944.

² U. S. patents 2122419, 2122420, 2122446.

The electrodeposition problem was solved by Rathenau with his contact cathode. This is a round steel bar or pipe which is placed vertically in the cell and can be moved up or down. It may be water cooled. In operation it is set so that its lower end just touches the surface of the bath. The resultant high current density raises the temperature in the neighborhood of the cathode above the melting point of calcium, causing the metal to be deposited in the molten state. If conditions are correct, the calcium wets the steel and will adhere to it when it is raised. This is done slowly, and the metal solidifies a short distance above the bath level. Continuation of the upward movement causes more metal to be drawn up and to solidify so that a vertical rod of calcium is slowly built up. The lower end of the calcium, therefore, quickly becomes the real cathode, the steel serving merely as a lead for the current. The metal, as it leaves the bath, becomes coated with a thin layer of molten electrolyte which soon solidifies and serves as a protective coating. As electrolysis proceeds, the

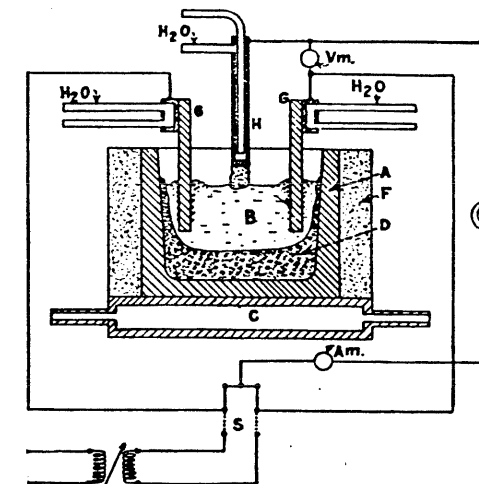


FIG. 4.—Improved Rathenau cell.

lower end of the calcium becomes larger until an equilibrium size is reached, with the result that the deposited metal acquires a roughly conical shape. Because of this shape, the lump of crude metal is known as a "carrot."

The speed with which the cathode is raised is critical. If it is much too great, contact is broken immediately. If not quite so great, the deposit becomes smaller in diameter, the current density and temperature rise, the metal stays molten farther above the bath level, convection currents become more violent, and eventually contact is broken. If too slow, the temperature drops below the melting point of the metal and a spongy deposit is obtained. In the early days of calcium production, regulation of the cathode was manual, but recently automatic controls have been developed.

When the cathode has reached the end of its travel upward, electrolysis is stopped, the carrot is removed, the steel cathode lowered, and the process repeated. The carrots produced from the latest cells range in size from 7 to 14 in. in diameter and 7 to 25 in. in length.¹

The anode material is graphite. Some experimenters have recommended that the cell lining be made of this material and used as the anode, but Brace² used separate anodes which could be moved about to control the voltage drop and therefore the

¹ KINZEL, *Mining Met.*, Vol. 22, p. 488, 1941.

² *Trans. Electrochem. Soc.*, Vol. 37, p. 465, 1920.

temperature of the bath to some extent independently of that at the cathode. The largest United States producer adopted this idea in a pilot-plant cell, but it is not known whether it is being used on a large scale.

The electrolyte used in commercial European practice is a mixture of calcium chloride and fluoride. Some workers have recommended potassium chloride, instead of calcium fluoride, while Frary, Bicknell, and Tronson,¹ and Brace prefer the pure chloride on the basis that the melting point of the bath should not be too far below that of the metal. According to Mantell and Hardy,² the operating temperature of the bath is between 780 and 800°C. They also state that the bath must be skimmed at intervals and occasionally discarded owing to accumulation of impurities.

Cells with capacities up to 10,000 amp. are now in operation in the United States. They are probably more efficient than the smaller European cells which have an

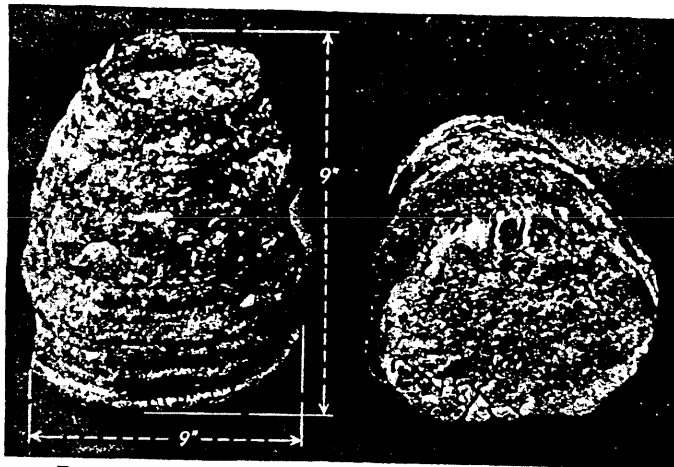


FIG. 5.—A calcium carrot. (Courtesy of Dr. A. B. Kinsel.)

energy consumption of about 23 kw.-hr. per lb. of metal produced. However, a higher energy consumption is inherent in this process owing to the large potential drop at the contact cathode.

The present calcium cell has a number of disadvantages in addition to the high energy consumption. The large production of heat in the cell seriously limits its size, as this heat must be radiated. Because of the contact cathode, the top of the cell cannot be closed in and the chlorine must be swept out with a current of air. The dilution of the chlorine makes it unavailable for liquefaction, an important item since about 1.75 lb. are produced per pound of metal, and in addition presents a serious disposal problem. Furthermore, the current of air not only carries off considerable quantities of electrolyte as spray, but its water vapor and oxygen are probably chiefly responsible for the deterioration of the bath.

The carrots produced in the United States³ contain only about 85 per cent metal, most of the remainder being electrolyte. To remove this they are melted and cast into various shapes in an atmosphere of argon. The product contains 95 to 97 per cent calcium. A higher grade of metal is produced by distillation in a retort at high vacuum. Sodium in the crude metal caused trouble in this operation by distilling over with the calcium and igniting when the retort was opened, but this difficulty was soon overcome through experience.

¹ *Trans. Electrochem. Soc.*, Vol. 18, p. 117, 1910.

² *Metals & Alloys*, Vol. 10, p. 55, 1939.

³ BAGLEY, *Chem. Eng. News*, Vol. 22, p. 921, 1944.

Production and Prices.—Prior to 1939, practically all the calcium used in the United States was imported from France. The amount of these imports, taken from the "Minerals Yearbook," are shown in Table 3. Production in the United States began in the summer of 1939, has grown rapidly, and is now probably more than

TABLE 3.—IMPORTS OF CALCIUM

Year	Weight, Pounds
1937	23,767
1938	41,299
1939	41,718
1940	11,900

500,000 lb. per year. Prices have remained steady for the last few years at \$1.25 a pound for 97 to 98 per cent metal in ton lots. Available forms are slabs of various sizes and cylinders, either with or without a central steel pipe, and turnings.

Uses.—Calcium has a number of important uses. It is added to magnesium alloys to the extent of about 0.25 per cent to refine grain, reduce tendency to take fire, and to simplify heat-treatment. Its property of reducing the tendency to take fire is so pronounced that specifications placed very low limits on the amount permissible in incendiary-bomb alloy. Its effect on heat-treatment is observed in those alloys containing zinc. In its absence, a two-stage treatment is necessary, one at a temperature below the melting point of the zinc-bearing constituent to dissolve this, and another at a higher temperature to dissolve the aluminum. In its presence, only the high-temperature treatment is necessary.

Calcium is added to lead to harden and strengthen it. Its solid solubility in lead is 0.10 per cent at the melting point and decreases rapidly with the temperature with the result that precipitation hardening takes place. The alloy, which contains less than 0.25 per cent calcium, is used for cable sheaths and has been recommended for storage-battery grids and other purposes. Master alloys containing up to 5 per cent calcium, the balance lead, are on the market and are made by electrolysis of fused calcium chloride with a molten lead cathode, or from lead and calcium carbide.

Calcium and magnesium are used in the Betterton process for removing bismuth from lead. They form compounds with bismuth, which are insoluble in lead just above its melting point and form a dross which is skimmed off.

The metal is an excellent scavenger. It reacts readily with oxygen, nitrogen, sulphur, carbon, and many of their compounds. It has therefore been recommended as an addition to both ferrous and nonferrous alloys. Its affinity for oxygen makes it a powerful reducing agent, and Marden and Rich have worked out a process in which it is used to reduce the oxides of vanadium, uranium, thorium, and other refractory metals. Calcium chloride is added as a flux. The metals produced are malleable and ductile and fully equal in properties to those made by the action of sodium on the anhydrous chlorides which are difficult to prepare and to handle.

Calcium hydride is being made commercially by the action of hydrogen on the metal and is being used for the reduction of refractory oxides, such as those of titanium, zirconium, and uranium, to produce commercial grades of these metals and their alloys with the more common metals.

BARIUM

Barium is the eighteenth most abundant element, being present in the earth's crust to the extent of about 0.04 per cent. Its principal minerals are the sulphate, barite, and the carbonate, witherite. Witherite is preferred as it is readily soluble in acids to form other barium salts, but barite is more available. To produce other barium salts from barite, it is heated in a rotary kiln with carbon to reduce it to the

sulphide which is dissolved in water and treated with carbon dioxide gas or with soda ash to precipitate the carbonate. As already mentioned, barium carbonate is not readily converted to oxide. To accomplish this, it is mixed with carbon and heated, with the result that the carbon dioxide is reduced to monoxide and goes off.

Barium chloride is readily prepared by dissolving the carbonate in hydrochloric acid. It can be readily prepared in the anhydrous state as it is not nearly so soluble as calcium chloride and crystallizes with only two molecules of water which can be driven off at a low temperature without hydrolysis.

Metallurgy. 1. *Thermal.*—Barium can be produced by reduction of the oxide with aluminum in an evacuated retort. Guntz¹ used this method in 1906. A reference to a Russian article² gives some details of the process. A vertical retort is equipped with a water-cooled condenser and heated by an electric furnace. The apparatus is 23 cm. in diameter at the bottom and 50 cm. high. The temperature of distillation is 1050°C. and the yield per batch, 304 g. of metal containing 99.41 per cent barium and a total of 0.071 per cent copper manganese and aluminum. The condensed barium is removed in a carbon dioxide stream and sealed in iron cylinders. The same apparatus can be used for production of barium, magnesium, strontium, and calcium and their alloys.

The barium is usually recovered as a solid in this process, but a recent patent,³ specifies keeping the condenser at a temperature between 730 and 800°C., whereby the metal is condensed to liquid and, still under vacuum, allowed to run to a receiver where it solidifies. Another French patent⁴ specifies a ratio of barium oxide to aluminum of 4:2 and states that up to 2 per cent barium fluoride may be added to promote the reaction. The patents to which reference was made in discussing the reduction of calcium by aluminum also cover barium.

Danner⁵ describes a variation of this process in which an oxide containing about 10 per cent barium peroxide is used. The reduction reaction is carried out in a separate vessel, the heat required being supplied by the reaction of the peroxide with part of the aluminum. The barium is recovered from the resulting sintered mass by distillation *in vacuo*.

Matignon⁶ found that barium oxide could also be reduced by silicon. He used a mixture containing three parts of the oxide to one of silicon, formed the mixture into briquettes, and heated at 1200°C. in an evacuated steel tube. The metal obtained was 98.5 per cent pure, and the residue in the retort contained barium silicate. In another experiment, he used 90 per cent ferrosilicon with equally good results.

All the patents referred to above also cover the use of silicon as a reducing agent. The ratio of barium oxide to silicon is given as 4:1.⁴

2. *Electrolytic.*—As in the case of calcium, barium has not yet been deposited from aqueous solutions. However, an amalgam can be made, and Guntz⁷ first prepared a comparatively pure barium metal in this way. He heated the amalgam to drive off most of the mercury, heated the residue in hydrogen to convert the barium to the hydride and drive off the rest of the mercury, and finally decomposed the hydride *in vacuo* at a high temperature, the barium metal condensing on a water-cooled surface.

Neumann and Bergve⁸ state that they produced metallic barium from fused barium chloride, using a contact cathode similar to that used for calcium, but give

¹ *Compt. rend.*, Vol. 143, p. 339, 1906.

² *Chem. Abstracts*, Vol. 34, p. 7181, 1940.

³ French patent, 831083 to I. G. Farben.

⁴ French patent, 831598 to I. G. Farben.

⁵ *Jour. Am. Chem. Soc.*, Vol. 46, p. 2382, 1924.

⁶ *Compt. rend.*, Vol. 156, p. 1378, 1913.

⁷ *Compt. rend.*, Vol. 141, p. 1240, 1905.

⁸ *Z. Elektrochem.*, Vol. 20, p. 187, 1914.

no details on the procedure. It is probable that all the barium on the market is being produced by aluminum or silicon reduction.

Production and Prices.—No information is available as to the production of barium or current prices.

Uses.—Barium, either alone or as an alloy with magnesium or aluminum, is widely used as a "getter" to remove residual gases from electron tubes. It is stated to be ten times as efficient as magnesium for this work. A barium-nickel alloy is being used for the terminals of spark plugs.¹ The alloy contains up to 0.2 per cent barium and reduces the potential required to produce a spark across the gap. An alloy containing about 1 per cent barium has been found to be an efficient emitter of electrons when heated and for this reason has been suggested for use in vacuum tubes. Nickel alloys containing up to 1½ per cent barium are ductile and may be easily rolled or drawn into fine wire or ribbon. A recent use for barium is as a lubricant for rotating anodes in X-ray tubes. Ordinary lubricants cannot be used as the temperature is high, about 600°C., and their vapors cannot be tolerated in the tube. Barium has a low vapor pressure at that temperature and shows excellent lubricating qualities.

STRONTIUM

Strontium is about 40 per cent as abundant as barium, and like that metal, its chief minerals are the carbonate, strontianite, and the sulphate, celestite. Again the sulphate is more abundant and serves as the major source of strontium salts.

Before 1940, practically all the celestite used in the United States was imported from England as the domestic deposits were either remote from transportation or of low grade. However, since that time domestic sources have been developed and are supplying the increased demand due to the war.

Strontium salts are manufactured from the minerals by the same methods used for barium salts. Strontium carbonate is more readily converted to the oxide than barium carbonate, and the operation is conducted in the same manner as with limestone.

Metallurgy. 1. *Thermal.*—The methods used for barium can be used equally well for strontium. Guntz and Galliot² reduced the oxide by mixing the finely ground material with powdered aluminum and heating in an evacuated iron tube for 4 hr. at 1000°C. Metal of 99.4 per cent purity was recovered as a crust, with a yield of 76 per cent. The method in which strontium peroxide is added to the charge and the reaction and distillation are carried out in separate containers has been used commercially.

2. *Electrolytic.*—Strontium amalgam can be made from aqueous solutions, but it has not yet been found possible to deposit the pure metal.

Neumann and Bergve³ prepared strontium by the electrolysis of a fused mixture containing 84 per cent strontium chloride and 16 per cent potassium chloride. They used the contact electrode and secured a current efficiency of 80 per cent.

Production and Prices.—There is no available current information on these subjects. Some fourteen years ago, a figure of \$100 a pound was published. Four years later it was stated that the price was still over \$30.

Uses.—Strontium occupies the same position among the alkaline-earth metals as rubidium does among the alkalis, *i.e.*, it is intermediate in its properties between barium and calcium. About fifteen years ago, metallic strontium was in comparatively large demand as a "getter" for radio tubes, but it has since been supplanted by barium and its importance as well as its production has fallen off.

¹ *Trans. Electrochem. Soc.*, Vol. 66, p. 85, 1934.

² *Compt. rend.*, Vol. 151, p. 813, 1910.

³ *Z. Elektrochem.*, Vol. 20, p. 187, 1914.

CHAPTER IV

ARSENIC

BY WALTER C. SMITH¹

Arsenic was not recognized as a metallic element until it was isolated by Schroeder in 1694; several of its compounds, however, were known from antiquity and were called arsenic. The name arsenic is used even today when the arsenious oxide is meant. Metallic arsenic is not used in the arts to a great extent, while the arsenious oxide (white arsenic of commerce) has many uses.

Physical Properties.—The metal has a steel-gray color and shows a brilliant luster on fresh fracture; it is known in both the crystalline and amorphous states. The crystalline form is very brittle. Other physical properties are: atomic weight, 74.96; number by Moseley's arrangement, 33; specific gravity, (crystalline) 5.727, (amorphous) 4.71; fracture, coarsely crystalline; crystallization, hexagonal; melting point, red heat under pressure in the absence of oxygen; boiling point, volatile at 450°C. without melting; specific heat, (crystalline) Sm, 0.083; (amorphous) Sm, 0.0758; latent heat of sublimation, 60 cal. per g.

Chemical Properties.—Arsenic is not changed in dry air, but in moist air it loses its color and brilliancy and slowly changes into arsenious oxide. It burns with a bluish-white flame when heated in air and gives off heavy white fumes of arsenious oxide, which have a characteristic odor resembling garlic.

Nitric acid oxidizes arsenic to arsenious oxide and then to arsenic oxide. Aqua regia yields a mixture of arsenious and arsenic compounds. Arsenic is soluble in hot concentrated sulphuric acid, but dilute acid does not attack it. Hydrochloric acid attacks it in the presence of air, feebly, to form arsenious chloride. It combines directly with chlorine to form arsenic chloride. It also combines directly with sulphur, when heated, to form arsenic sulphide. Metallic arsenic yields potassium arsenate when heated with niter or potassium chlorate.

In solution, silver will replace arsenic and vice versa, depending upon conditions, but Fe, Ni, Co, Cr, and Mo will not replace arsenic to a notable extent under any conditions. The single potential of arsenic (vs. calomel electrode = 0.577 volt) was found to be 0.55 in an AsCl₃ solution of 1 g.-equivalent of arsenic per liter and 0.54 volt in a corresponding solution of AsI₃.

Uses.—As already indicated, only limited quantities of metallic arsenic are used. A small amount of arsenic is added to lead in making lead shot, as it tends to prevent the formation of imperfect shot when the molten metal is dropped in the shot tower. A very small percentage of arsenic added to steel produces a metal that will take an extremely high polish. Arsenical copper is claimed to possess superior properties to pure copper for certain rolling and drawing operations.

The chief arsenic compound of commerce is the arsenious oxide (As₂O₃), trioxide, or white arsenic. This is used in the manufacture of glass, in the textile and paint industries, and in the manufacture of weed killers, insecticides, and medicines.

A small amount of arsenic is added to the low tin wiping solders to improve their working properties. Arsenic is added to lead, antimony, and silver alloys for use as

¹ Metallurgist, Cerro de Pasco Copper Corp., New York.

insoluble anodes in the electrolytic recovery of copper from acid sulphate solutions to increase the anode life. *Anode life*

Arsenical preparations furnish the most effective means of control against the cotton boll weevil, the cotton worm, the codling and the gypsy moth, and they are used for soil treatment to destroy Japanese beetle grubs. It is estimated that insecticides take 68 per cent of the arsenic used in the United States; weed killers, 19; glass manufacture 3; wood preservatives, 2; miscellaneous, including arsenical drugs, 1; exports, 7 per cent. Approximately 60,000,000 lb. of lead arsenate, 40,000,000 lb. of calcium arsenate, 2,000,000 lb. of paris green, besides important quantities of London purple and sodium arsenite, make up the first item.

Sources of Arsenic.—Arsenic, while not abundant, is one of the most widely disseminated of all the metallic elements. It has been found in a number of places in the native state, usually associated with other metals. It occurs as mispickel, or arsenopyrite, in many cobalt and cobalt-silver ores. Nearly all pyrite and sulphide ores of copper and lead contain more or less arsenic, and it is from these latter ores that the bulk of the American supply of arsenic is derived as a metallurgical by-product. The most important American producers of arsenic are listed as follows:

Company	Location	Source of Arsenic
Am. Smelting & Ref. Co.	Denver, Colo.	By-product lead smelting
Am. Smelting & Ref. Co.	Tacoma, Wash.	By-product copper smelting
Anaconda Copper Mining Co.	Anaconda, Mont.	By-product copper smelting
U. S. Smelting Co.	Midvale, Utah	By-product lead smelting
Rare Metal Products Co.	Belleville, N. J.	Arsenic sulphides

Metallic arsenic is produced by the sublimation of mispickel or leucopyrite in the absence of air, and by the reduction of arsenic trioxide with charcoal in cast-iron or steel retorts. The temperature and the pressure in the condensers have to be carefully controlled in order to yield the crystalline arsenic.

Previous to 1914 little or no metallic arsenic was made in the United States; about 50,000 lb. were imported annually, principally from Germany. After the First World War cut off the German supply, the Hoskins Process Development Co. of Chicago, Ill., began the manufacture of metallic arsenic to supply the American market. The arsenic of 99.5 per cent grade is made by the reduction of commercial arsenic trioxide with charcoal in a battery of four gas-fired furnaces as shown. Three of the furnaces take a charge of about 200 lb. each, and the fourth furnace holds 450 lb. of charge.¹

The charge is mixed in a rotary mixer in the proportions of 1 lb. of charcoal to 4 lb. of arsenic trioxide. The capacity of the plant is 250 to 300 lb. per day, or not less than 4000 lb. of metallic arsenic per month.

The furnaces are built of steel pipe, surrounded by firebrick, enclosed in a steel jacket and supported on a pipe frame. The charging end of the retorts is sealed with a clay gasket in which is embedded a ¼-in. copper water pipe. The cooled surface condenses arsenic vapor and seals any leaks in the clay gasket. At the back of and attached to the retort is a water-cooled condenser, which is vented by means of a water seal so as to allow the escape of the uncondensed gases. Figure 2 shows the left side of one of the furnaces. Two condensers are shown in the background of Fig. 1.

¹ JONES, *Chem. & Met. Eng.*, Nov. 17, 1920.

The period of operation for the large furnace is about 10 hr., and for the smaller furnaces 7 hr. The gas is then shut off, and the retort and the condenser are allowed to cool before the condenser is opened for the removal of the metallic arsenic. Figure 3 shows the discharge end of one of the furnaces. The metallic arsenic is removed from the condenser with a bar and hammer, and is then ready for packing and shipment.

The advent of the Second World War again stopped importation of metallic arsenic from Germany. During December, 1939, the Anaconda Copper Mining Co. began production of metallic arsenic from arsenic trioxide. The plant erected for the purpose consists of six cast-iron retorts, each fitted with a condenser consisting of a condenser tee flanged to the retort and flanged to a vertical water-cooled steel-plate condenser chamber. Each retort is horizontally supported and is enclosed with firebrick. The condensers are heated by direct gas firing. The end of the retort and of the condenser tee are closed with flanged covers bolted to the retort and con-

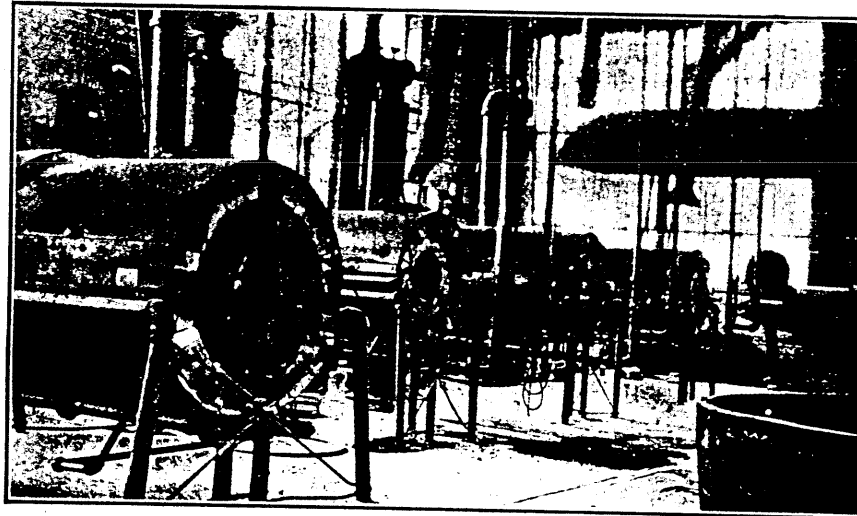


FIG. 1.—Arsenic furnaces, with condensers in background.

denser tee with fire-clay gaskets, in which is embedded a small-diameter copper pipe for water cooling.

The retorts are charged in batches through the end with a mixture of white arsenic, the trioxide, and charcoal. The arsenic trioxide is reduced to metallic arsenic in the retort and together with some white arsenic is volatilized and is largely condensed in the form of coarse gray crystals of metallic arsenic on the retort and tee covers. A part of the volatilized metallic arsenic passes into the condenser where it deposits on the condenser walls. The condensed metal is barred down frequently and falls into the hot tee and is again volatilized. Eventually, about 80 per cent of the arsenic in the charge is recovered from the retort and tee covers in the form of coarse crystals of metallic arsenic which are packed in airtight sealed cans for shipment.

Production of White Arsenic.—The production of white arsenic is generally carried out in two stages: the production of a crude white arsenic, followed by a refining of this crude material. When arsenic-bearing materials, in which the arsenic exists in the reduced state, are roasted, the arsenic is volatilized and passes off with the gaseous products. Arsenic trioxide begins to condense at 218°C.; hence the flue products caught in the cooler parts of the flue system carry considerable arsenic. More or less

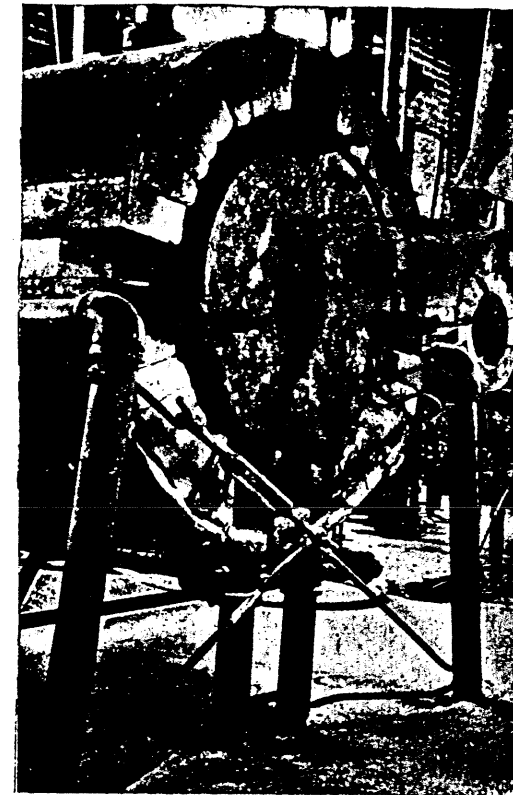


FIG. 2.—Side of arsenic furnace.



FIG. 3.—Discharge end of furnaces.

dust carried by the gases and other volatile materials can contaminate the arsenic trioxide, and these are removed in the refining operations.

The roasting operations may be carried out in muffle, reverberatory, or one of the various types of roasting furnaces; coke, gas, or oil is used for fuel in reverberatory or roasting furnaces in order to reduce the danger of contamination of the product with soot. The crude arsenic trioxide is collected in cooling flues, baghouses, or by Cottrell precipitators.

Crude White Arsenic from Metallurgical Products.—The arsenic carried by lead and copper ores is concentrated during the roasting and smelting operations in the flue products, which are caught in the cooler parts of the flue system. Lead baghouse dust, carrying 30 per cent arsenic, and copper furnace and roaster dusts, carrying 20 to 30 per cent arsenic, are not uncommon. The arsenic in these dusts exists largely in the form of the trioxide (As_2O_3).

At one of the American plants the baghouse dust, carrying about 30 per cent arsenic, is mixed with a small quantity of fine pyrite or low-grade lead sulphide concentrates and is fed to the hearth of a Brunton roasting furnace. The pyrite is added to the dust in order to prevent the formation of nonvolatile arsenites in the residue from the roast, and it also gives a clinkered residue which makes a suitable blast-furnace feed. The Brunton furnace volatilizes 75 to 90 per cent of the arsenic in the dust which is charged to it. The gases from the Brunton furnaces pass through a cooling flue built in the form of a number of connecting rooms or chambers. Brick is usually employed in the construction of these chambers, or kitchens, as they are called. The temperature of the gas in the cooling flue is so regulated that it enters the first kitchen at approximately $220^\circ C.$, and by the time it reaches the last kitchen it has dropped to $100^\circ C.$, or less. The crude arsenic trioxide collects in the kitchens and is removed at the end of the campaign for refining. This crude arsenic trioxide should contain 90 to 95 per cent As_2O_3 .

The crude As_2O_3 is resublimed in order to remove impurities; this operation is repeated until the desired purity is obtained. Reverberatory furnaces are used for this work and are fired with gas or coke. The furnace gases pass through settling chambers and then to the kitchens, where the refined arsenic trioxide is collected. The product should contain over 99 per cent As_2O_3 .

The main source of arsenic at Anaconda is in Butte copper ores. The concentrates from these ores average approximately 2.0 per cent As. The roasting and smelting operations eliminate a very considerable portion of the arsenic into the flue system where it becomes considerably concentrated in the dust collected at the Cottrell treaters and in the upper portion of the main flue. The Cottrell dust and the arsenic-enriched portion of the main flue dust constitute the feed to the arsenic roasters.

Arsenic Roasting Plant.—Three rows of McDougal roasters in No. 1 roaster building have been remodeled into three sets of arsenic-roasting furnaces and condensing chambers. A set consists of four 16-ft. six-hearth furnaces connected in series. The first, or roasting, furnace is gas-fired on the third and fifth hearths and is equipped with a specially designed apron feeder for charging the dust. The remaining three furnaces serve as condensing chambers to collect the condensed arsenic in the form of a crude As_2O_3 product. The inside hearths have been removed and a central vertical partition installed. This partition has an opening at the bottom to permit the passage of the gases. The gases enter each condenser at the top, pass down one side of the partition and up the other, leaving at the top to enter the top of the next condenser and so on to their exit through connecting flues and a dust chamber to the flue system. The bottom sets of arms have been left in each condenser and are operated periodically to remove the collected arsenic, which is sent to the refining

furnaces. The roasting furnaces are operated at a temperature of approximately $650^\circ C.$, as higher temperatures cause fusion of the condensed arsenic in the condensers. Experience has proved that 50 per cent As_2O_3 is the maximum permissible in the feed to the roasters if fusion is to be prevented. Arsenical dusts of high arsenic content are diluted with fine flue dust. It has been found that improved results are obtained when coal to the amount of 10 per cent of the weight of the dust is mixed with the roaster feed.

The roasters yield a residue containing about 5 per cent As_2O_3 , which is returned to the reverberatory furnaces for the further recovery of copper and the elimination of arsenic into the flue system.

The roasting furnaces have a capacity of about 50 tons of charge per 24 hr. and yield a crude arsenic trioxide assaying about 90 per cent As_2O_3 .

Refining Plant.—Two refining furnaces of the reverberatory type have been installed. Each furnace has an over-all length of $36\frac{1}{2}$ ft. and a width of 14 ft.; the

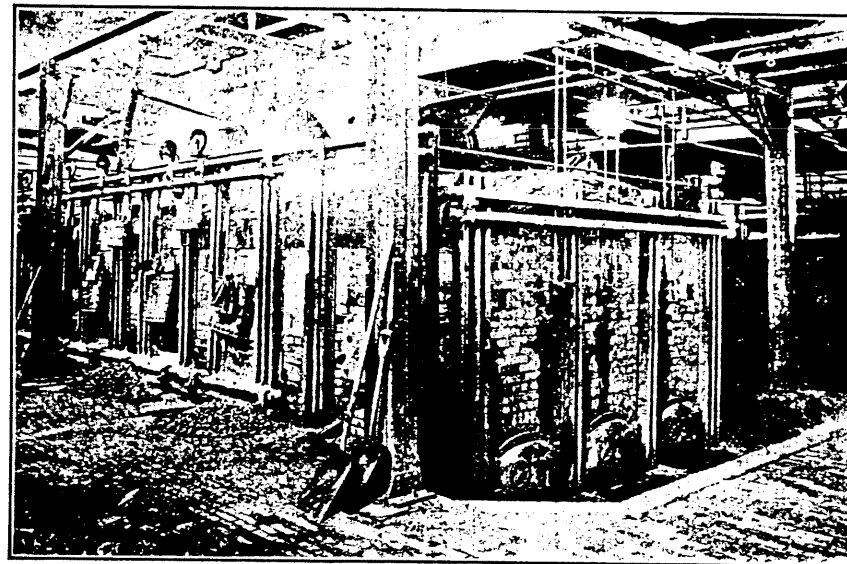


FIG. 4.—Arsenic refining furnace.

hearth is $26\frac{3}{4}$ ft. long and 12 ft. wide. The main hearths are made of cast-iron plates. Two fireboxes are used, one at the back of the furnace, whose hot gases pass under the cast-iron hearth and back over its top, and the other at the front of the furnace, whose gases pass only over the hearth.

The charge consists of 8 tons per furnace day of the 90 per cent As_2O_3 crude arsenic from the arsenic roasters. The charge is dropped to the hearth through openings in the roof and is spread out with rables; part of the charge is dropped during the afternoon shift and the balance during the night shift. A thin layer of crushed rock is spread over the hearth before charging the furnaces to facilitate the removal of the residue after the arsenic has been volatilized. A special crew cleans the hearths on the day shift. Each refining furnace will treat 30 tons per day, when treating very high-grade dust or when rerefining. High-grade material is dropped on all three shifts, and the residue is removed once in 2 or 3 days. A temperature of $550^\circ C.$ has been found to give the best results in these furnaces. A draft of 0.05 in. of water

gives satisfactory results. The volatilization of about 80 per cent of the arsenic in the 90 per cent As_2O_3 material fed to the furnace gives the most economical operation. The refining-furnace residues are smelted in the stack reverberatory.

Condensing Kitchens.—Three sets of chambers are used for handling the gases from two refining furnaces, two of these chambers being used while the third is being cleaned. Each chamber is approximately 225 ft. long and is divided into 39 kitchens. The kitchen nearest to the furnace is larger than the others and is used for settling the nonarsenical dust. Its temperature is about $295^\circ C.$, or above the condensation temperature of As_2O_3 . The gases cool as they pass through the kitchens by radiation

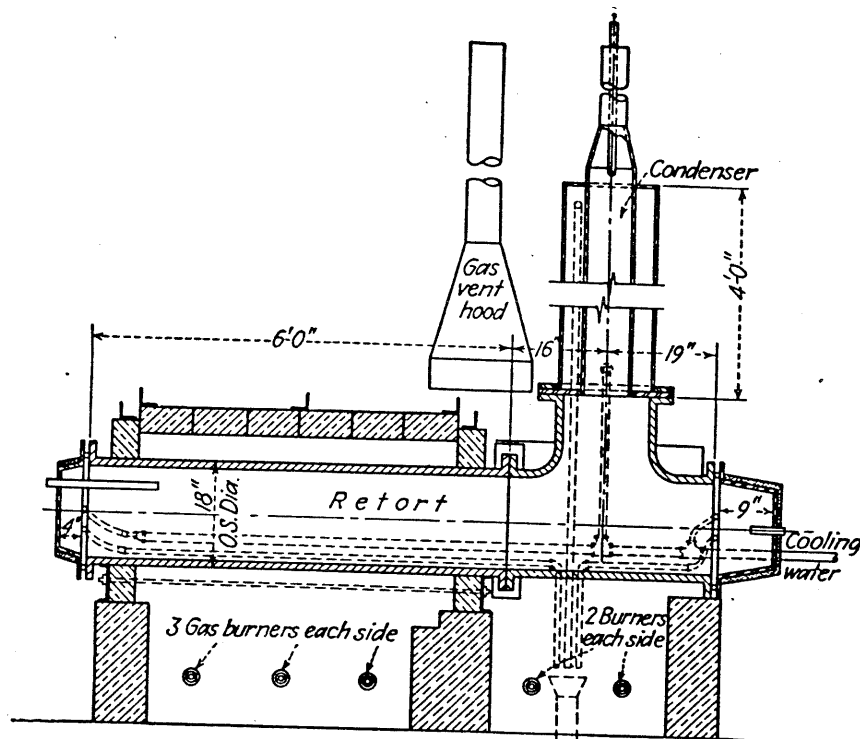


FIG. 5.—Modern refining furnace. (Courtesy of Anaconda Copper Mining Co.)

and leakage and leave the system at 90 to $160^\circ C.$ Most of the arsenic settles out in those kitchens which have temperatures from 180 to $120^\circ C.$ The kitchens nearest to the furnace contain a fused or amorphous arsenic, black in color, and carrying about 95 per cent As_2O_3 . This material is rerefined. The material in the succeeding kitchens increases in arsenic content to 99.9 per cent As_2O_3 , and is white and crystalline. The grade of the dust diminishes in the last kitchens, and changes to a fine white powder.

Packing.—At the end of each refining campaign the kitchens are sampled, and the samples are run for total arsenic and soluble arsenic. The product is then graded and packed in barrels of 500 lb. each; it is made into 50,000-lb. lots and sold as white soluble, white insoluble, or crude arsenic. The capacity of the packing room is 18 tons per 8-hr. day. The white insoluble arsenic can be changed to the white soluble by rerefining if market conditions demand.

Manufacture of Arsenic Trioxide from Arsenical Pyrite.¹—The arsenical pyrite is crushed by jaw crushers and is then ground in ball mills. The ground product is washed to remove as much foreign matter as possible, and dried. The drying was formerly done on the top of the roasting furnace, but this method cools the furnace and reduces the roasting efficiency. The drying is done in a mechanical drier, which is equipped with a screw conveyer for stirring and progressing the charge.

The dried concentrate is charged to the top of a roasting furnace of the MacDougall type, 18 to 30 ft. high and 10 to 16 ft. in diameter. The rabble arms rotate at a speed of 5 r.p.m., but even at this speed some dust is carried out of the roaster with the gases, and this dust must be separated from the gases before they pass to the condensing chambers. This is done by a dust separator placed at the gas outlet of the roasting furnace. This separator consists of an insulated chamber containing two rotating screens of fine mesh provided with revolving brushes for cleaning. This arrangement removes nearly all the solid matter in the gases and offers but little resistance to the flow of the gases. The cleaned gases are then drawn by a fan through the condensing chambers.

The condensing chambers are made of sheet lead and are divided into a number of smaller compartments by sheet-lead baffles which increase the condensing surface. Water sprays are introduced into the chambers to facilitate the condensation of the arsenic trioxide and to flush the condensed material out of the chambers into a collecting tank. Lead is the only metal that will withstand the action of the sulphurous acid generated from the sulphur in the concentrate.

The mixture of water and arsenic trioxide is then filtered in vacuum filter tanks, and the moisture content is reduced to 20 to 25 per cent by the addition of some dry arsenic trioxide. It is then passed through a rotary drier, which is lined with porcelain to prevent sticking to the sides of the drier. The drying temperature employed is about $180^\circ C.$, in order to prevent the loss of arsenic by sublimation during drying.

The crude arsenic trioxide is refined by sublimation. Furnaces 10 to 14 ft. in diameter, equipped with cast-iron hearths and rotating rabbles, are used for this operation. The crude arsenic trioxide is charged to the furnaces through openings in the roof. The proper temperature has been found to be $245^\circ C.$ Approximately 70 parts of fuel are required for each 100 parts of refined arsenic trioxide.

The final condensation takes place in lead-lined wooden chambers containing baffles and placed over a trough that carries a porcelain screw conveyer for the removal of the collected material. About 0.65 lb. of arsenic trioxide is condensed per square foot of condensing surface. The exit gases from the condensing chambers pass to a coke-filled scrubber, where the last of the arsenic is removed with water sprays. The finished product is finely powdered, perfectly white, and will assay 99.0 per cent As_2O_3 .

R. W. Bridges² gives the method used for the recovery of arsenic from the cobalt ores of Cobalt, Ont. The ores are crushed and then ground so as to pass 30 mesh in ball mills. The charge, with the proper fluxes, is smelted in 32×72 in. blast furnaces with capacities of 25 to 30 tons per day. The fluxes used are limestone and a low-grade siliceous ore. The products are flue dust and crude arsenic trioxide, slag, silver bullion, and speiss. The flue dust and crude arsenic trioxide are caught in suitable settling and condensing chambers. The flue dust is returned to the blast furnaces, and the crude arsenic trioxide is sent to the arsenic refinery for retreatment. The slag is discarded if it carries less than 10 oz. of silver per ton. The silver bullion assays about 860 fine and is treated in a cupel furnace for 24 hr., after which treatment it averages 994 fine. The speiss—a typical assay of which is Ag, 1480 oz.; As, 31.3; Co, 25.2;

¹ *Ind. chim.*, p. 426-429, December, 1920.

² *Metallurgy of Cobalt, Ontario, Ores, Can. Mining Jour.*, Jan. 15, 1916.

Ni, 15.3; Fe, 16.1 per cent—is crushed, ground, mixed with 20 per cent NaCl and roasted in Edwards mechanical roasters having a daily capacity per furnace of 2400 lb. The roasted product is then leached with cold water to remove the undecomposed NaCl and soluble salts of cobalt, nickel, and copper, which have formed in the roasting operation. The residue is then leached with four successive batches of $\text{Na}_2\text{S}_2\text{O}_3$ solution to remove the silver. The cobalt, nickel, and copper are recovered from the water leach liquors and the leached residues. The crude arsenic trioxide is resublimed in the arsenic refining furnaces in the usual manner, producing an arsenic trioxide of 99.0 per cent.

Manufacture of Lead Arsenate.—A number of methods have been proposed for the manufacture of lead arsenate, the first step of which is the conversion of arsenic trioxide or a soluble arsenite into arsenic acid or a soluble arsenate. A fusion of arsenic trioxide with caustic soda or sodium carbonate and sodium nitrate yields sodium arsenate, which is then dissolved in water and mixed with the solution of a soluble lead salt, as the nitrate or acetate, the insoluble lead arsenate being precipitated. Chlorine gas will slowly convert a solution of sodium arsenite into sodium arsenate; it will also convert a mixture of arsenic trioxide and water into arsenic acid. Nitric acid and arsenic trioxide react violently to form arsenic acid; the gaseous products of the reaction contain considerable nitric acid and are generally sent to a condensing system for the recovery of this acid.

A patent¹ issued to Luther and Volck covers the formation of lead arsenate by roasting the combining parts in the presence of oxygen. Lead arsenite is formed and oxidized to lead arsenate by roasting in the presence of oxygen. The lead arsenite is produced by heating white arsenic with lead or lead oxide. It may also be formed as a mixture of lead arsenite and lead arsenate by heating red lead with white arsenic. Lead arsenate may be formed directly by roasting white arsenic with lead peroxide or lead nitrate or one of the lower oxides of lead with an oxidizing agent.

The Barstow and Cavanagh patent² consists in combining litharge with arsenic acid assisted by the action of a catalytic agent; the direct combination of arsenic acid and litharge is too slow to be of commercial value. The catalytic agent used is a small amount of either nitric or acetic acid.

U. S. patent 1398267, issued to John Kirby, Matthew S. Hopkins, and Charles B. Bernhart, of Reading, Pa., covers the use of sulphonic acids of the aromatic hydrocarbons as catalytic agents for the manufacture of lead arsenate from litharge and arsenic acid. The purity of the sulphonic acid used is nonessential, as the mixture of sulphonic acids obtained by the sulphonation of the commercial grades of hydrocarbons will act effectively. The lead arsenate produced by the use of these reagents possesses the physical requirements important for an insecticide, *viz.*, large bulk, good dispersion, proper adherence to the foliage treated, and effective insecticidal properties.

The preparation of the catalyst is carried on approximately as follows: A commercial grade of a suitable hydrocarbon, such as ordinary naphthalene, is sulphonated in the usual manner, the excess sulphuric acid is removed by precipitation with a soluble lead salt, and the clear liquor is separated by decantation or filtration.

A charge of 700 lb. of litharge is placed in a tank and agitated to keep the litharge in suspension in water. About 50 lb. of the mixed sulphonic acids is added, the quantity to be used depending upon the speed of reaction required and the physical properties desired in the product. Approximately 600 lb. of a 75 per cent arsenic acid is then slowly added. The temperature is raised to 160°F. The mass slowly changes in color to white as the litharge is converted to lead arsenate. Any excess of litharge is removed by the addition of more arsenic acid. The resulting mass of lead arsenate,

¹ U. S. patent 929962, Aug. 3, 1909.

² U. S. patent 1228516, May 5, 1917.

the lead salt of the sulphonic acid, and water may be washed and the lead arsenate pressed for use as paste or as powder after drying and grinding. The sulphonic acid liberated by the precipitation of the lead arsenate is available for further use as a catalyst.

Lead carbonate or basic lead carbonate can be substituted for litharge and a solution of a soluble arsenate for the arsenic acid.

Manufacture of Calcium Arsenate.—Calcium arsenate is manufactured by the method developed by the U. S. Department of Agriculture at Tallulah, La. This consists in the oxidation of arsenic trioxide to arsenic acid by means of nitric acid. The arsenic acid is then neutralized with sodium hydrate to form sodium arsenate, and calcium arsenate is precipitated by the addition of milk of lime to the solution of sodium arsenate. The calcium arsenate produced must have the necessary physical properties for use as an insecticide.

Calcium arsenate is also made by direct combination of arsenic acid and milk of lime under controlled conditions to yield a product of the required chemical and physical properties.

Precautions in Handling Arsenic Trioxide.—Arsenic trioxide is very poisonous, and considerable care must be exercised to prevent occupational poisoning. Ample draft in the furnaces and flue systems, proper ventilation in all parts of the arsenic plant, proper bathing facilities for the men, and the use of efficient respirators have greatly reduced the danger of arsenic poisoning. One American plant has successfully applied the pneumatic system to the removal of the arsenic trioxide from the kitchens.

CHAPTER V

ANTIMONY

BY CHUNG YU WANG¹ AND GUY C. RIDDELL²

History.—In point of use by man, antimony is one of the oldest of the metals. The natural sulphide was known to the people of ancient times. It was used by them as medicine and as an article of toilet for eyebrow painting by women of biblical times. A vase found at Tello, Chaldea, cast in metallic antimony discloses the fact that in about 4000 B.C. the Chaldeans knew the art of the reduction of the metal. A copper ewer and basin of the Fifth or Sixth Dynasty (about 2500-2200 B.C.), discovered in Egypt, was found covered with a thin coating of metallic antimony, thus showing that the ancient Egyptians knew something of the art of surface plating.

Basil Valentine, a German monk of the fifteenth century, and Agricola³ wrote of liquation, precipitation, and starring of regulus. Valentine gave distinct recipes for the preparation of antimony trichloride, basic chloride, trioxide, and potassium antimonate. In the fifteenth century, antimony was in use for printers' type, and in mirrors and bells. In the sixteenth century came its use as a medicine. Of the methods now obtaining in antimony metallurgy the precipitation of metal from sulphide by iron appears in writings of the seventeenth century (Ercker), and in the eighteenth century, the roast-reduction procedure came into use. In the early 1830's came the reverberatory furnace; in 1878, direct smelting in the blast furnace; in 1844, the French volatilization process; and in 1896, electrolytic antimony first appeared in the market.

Physical Properties.—Pure antimony is a silver-white shining brittle metal. Other physical properties are: atomic weight, 121.76; atomic number, 51; specific gravity, 6.6 to 6.7; hardness, 3.0 to 3.5; specific heat, 0.05; melting point 630.5°C.; latent heat of fusion, 38.84 cal. per g.; crystallization, hexagonal.

Other allotropic forms of antimony are explosive antimony, black antimony, and yellow antimony. Explosive antimony can be produced by electrolysis, using a bath of hydrochloric acid and antimony protochloride, with antimony metal as anode and platinum foil as cathode. This form of antimony, rubbed in a mortar, loudly detonates, giving off light and heat. Black antimony is another metastable amorphous form, produced when antimony metal vapor is suddenly cooled. This form of the element is more active chemically than the ordinary metallic form, being sometimes spontaneously combustible. At 100°C. it changes gradually to the ordinary metal; at 400°C. the change is sudden.

Yellow antimony, the most unstable of the several forms of antimony, is without any metallic property and corresponds to white phosphorus and yellow arsenic. This form, obtained by introducing oxygen into antimony hydride at -90°C., is of academic interest only. It changes into black antimony above -90°C., under ordinary light.

Chemical Properties.—Antimony has three valences, three, four, and five. Its chemical properties resemble those of arsenic, and it stands close to the zinc group,

¹ Director of research, Wah Chang Smelting & Trading Co., N. Y.

² Consulting engineer, New York.

³ "De re metallica," Vol. 12, 1557.

being closely similar to germanium. Antimony is but slightly oxidized at ordinary temperatures. On heating, however, the metal readily oxidizes to the trioxide. The metal is also readily oxidized by any salts that can easily give up their oxygen component, such as lead oxide and manganese peroxide. It also oxidizes in the presence of steam.

In acids, the metal is unattacked by dilute sulphuric, but forms antimonious sulphate in hot concentrated sulphuric. It is attacked by hydrochloric only when in a state of fine powder. In concentrated nitric, it is converted to the trioxide. In aqua regia it dissolves readily to form the pentachloride.

Mixed with niter and soda, antimony explodes on ignition. With alkaline nitrate and chlorate, the metal decrepitates, forming an antimoniate.

Some of the fundamental constants and chemical reactions germane to the metallurgy of antimony are now recapitulated, as follows:

Sb_2S_3 melts at 550° (Pelabon); at 540° (Wagemann); at 546° (Borgstrom)

Sb_2S_3 volatilizes, in the absence of air, between 650° and 917° (S. A. Chakhov and I. I. Slobodskai)

$Sb_2S_3 + 9O \rightarrow Sb_2O_3 + 3SO_2$; begins at 290°, rapid at 520°, and finishes at 560° (Saito); begins at 290°, if the size of the grain is 0.1 mm. in diameter, at 343° if 0.1 to 0.2 mm., and at 430° if 0.2 mm. (Friedrich); commences at 190°, energetically at 340°, and terminates at 445° (S. A. Chakhov and I. I. Slobodskai)

$Sb_2S_3 + 2Sb_2O_3 \rightarrow 6Sb + 3SO_2$; in a current of inert CO_2 gas, at 950° (W. R. Schoeller)

$x(Sb_2S_3) + y(Sb_2O_3) \rightarrow xy(Sb_4O_3S_2)$; fused under a layer of salt; at 517°

$Sb_2S_3 + Fe \rightarrow 2Sb + 3FeS$

$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2$; H = -687,000 cal.

$Sb_2S_3 + 3H_2O \rightarrow 2Sb_2O_3 + 3H_2S$; H = +26,700 cal.

$Sb_2S_3 + 5O_2 \rightarrow Sb_2O_3 + 3SO_2$; H = -389,900 cal.

$Sb_2O_3 + O \rightarrow Sb_2O_4$; at above 445° (Chakhov and Slobodskai)

$Sb_2O_4 + O \rightarrow Sb_2O_5$; commences at 900° and finishes at 1030° (Chakhov and Slobodskai)

$3Sb_2O_3 \rightarrow Sb_2O_5 + O_2$; at between 620 and 720° (A. Simon and E. Thaler)

$Sb_2O_3 \rightarrow Sb_2O_4 + O$; at between 750 and 800° (A. Simon and E. Thaler)

$Sb_2O_4 \rightarrow Sb_2O_3 + O$; at 930° (A. Simon and E. Thaler)

$5Sb_2O_3 + O \rightarrow 2Sb_5O_8$; at between 360 and 400° (C. T. Carnelley and J. Walker)

$2Sb_2O_3 + O \rightarrow Sb_4O_7$; at between 440 and 500° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_4O_7$; stable between 500 and 565° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_2O_4$; at between 565 and 585° (C. T. Carnelley and J. Walker)

$Sb_2O_3 + O \rightarrow Sb_2O_4$; stable at between 590 and 775° (C. T. Carnelley and J. Walker)

$2Sb_2O_3 + 3C \rightarrow 2Sb_2 + 3CO$; at red heat

$Sb_2O_4 + 4C \rightarrow 3Sb + 4CO$

$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$; between 502 and 596°

$Sb_2O_3 + 6H \rightarrow Sb_2 + 3H_2O$; at red heat

$Sb_2O_3 + 3CO \rightarrow 2Sb + 3CO_2$; at 500° (Watanabe)

Ores and Deposits.—There are found in nature upward of about 112 minerals containing antimony, but only a few of them, as arranged in Table 1, can be considered as antimony ore-forming minerals.

Speaking generally, antimony lodes are simple lodes, limited in strike and depth, and belonging to the mesothermal type of deposits. Usually their sizes are irregular, pinching off rapidly. Most of the well-known deposits in various parts of the world occur, either directly or indirectly, associated with igneous rocks. They are generally granites and rocks of intermediate acidity, such as diorites, quartz-diorites, monzonites,

and quartz-monzonites. The exceptions to the general association of igneous rocks are the metasomatic replacement deposits in limestone.

TABLE 1

Class of mineral	Name of mineral	Formula	Antimony, %	Specific gravity	Mode of occurrence
Sulphide....	Stibnite	Sb_2S_3	71.4	4.52-4.62	Hypogene
Oxide.....	Valentinite (rhombic)	Sb_2O_3	83.3	5-5.66	Supergene
Oxide.....	Senarmontite (cubic)	Sb_2O_3	83.3	5.22-5.30	Supergene
Oxide.....	Cervantite	Sb_2O_4	78.9	4.084	Supergene
Hydroxide..	Stibiconite	$Sb_2O_4 \cdot H_2O$	74.5	5.1-5.28	Supergene
Oxysulphide	Kermesite	$2Sb_2S_3 \cdot Sb_2O_3$	75.0	4.5-4.6	Supergene
Native.....	Native antimony	Sb	94-98	6.65-6.75	Hypogene
Mercury ore	Livingstonite	$HgSb_4S_7 (HgS \cdot 2Sb_2S_3 \cdot S)$	53	4.81	Hypogene
Lead ore....	Jamesonite	$Pb_2Sb_2S_5$	29.4	5.5-6.0	Hypogene
Copper ore.	Tetrahedrite	$Cu_8Sb_4S_7$	24.7	4.4-5.1	Hypogene

Market and Uses.—In 1935, the United States consumed 46 per cent of the antimony of the world, Great Britain 18, Germany 13.3, France 9.4, and Italy 3.6 per cent. The average price per pound of antimony from 1908 to 1938 was 11.6 cents (minimum 5 cents, maximum 45). Ore is generally bought on an agreed price per unit (United States unit being 20 lb., British 22.4 lb.). Antimony content of the ore is generally limited to a minimum of 50 per cent. Lead, bismuth, arsenic, copper, and zinc are considered objectionable impurities and are penalized if they are present above the following percentages: lead 0.3, arsenic 0.1, copper 0.1 per cent; zinc and bismuth are considered very objectionable impurities if present in more than traces.

The trade specification for the metal or regulus is that it shall contain a minimum of 99 per cent antimony and not more than 0.3 per cent arsenic and show the usual bright "stars" on the surface.

Uses.—The principal uses of antimony, arranged in the order of magnitude of consumption, are as follows:

I. METALLURGICAL USES, in the form of alloys.

Batteries.—The largest use of antimony—normally about 30 per cent of the total United States consumption—is in the manufacture of grids in storage batteries, as used principally in automobiles. The percentage of antimony in storage-battery grids ranges from 5 to 12.

Bearings.—For bearing purposes the quantity of antimony required amounts to about 20 per cent of the annual consumption in the United States. Bearing metal is sometimes known as white metal. There are two types of white metal, the tin-base and the lead-base; the former is known commercially as "babbitt metal" or "babbits." The genuine babbitt metal contains generally less than 10 per cent antimony and the lead-base white metal less than 15 per cent antimony.

Type Metal.—This is essentially an alloy of lead, antimony, and tin, containing up to about 30 per cent Sb.

Britannia Metal and Pewter.—Britannia metal is practically an alloy based on tin with antimony in variable proportions and smaller quantities of copper, zinc, lead, bismuth, or other metals. Pewter, an alloy of tin-antimony-copper, resembles high-grade Britannia metal.

Ammunition.—The general composition of shrapnel bullets is 12 to 15 per cent antimony, the balance is lead.

Cable Sheathings.—Cable sheathings are made of lead hardened by 0.75 to 1.00 per cent antimony.

Hard Lead.—Hard lead is simply antimonial lead. The antimonial content of the lead depends upon the use to which the metal is put, the percentage ranging from 6 per cent or lower for rolled sheets for linings and roofing to 28 per cent for special purposes, such as nozzles.

II. CHEMICAL USES.

Enameling.—As an opacifying agent for white enamels, antimony trioxide has almost completely replaced tin oxide, mainly because of the high price of the latter.

Pigments.—1. "Antimony white" is the trioxide of antimony which is formed as a very fine powder in the flues and dust chambers of antimony-roasting furnaces. It can be collected in this form and used without further treatment for certain paint purposes, but a specially ground and prepared oxide called Timonox is produced in England, of superior texture, opacity, and whiteness, which has become of great usefulness among pigments.

2. "Antimony black" is metallic antimony deposited electrically or chemically as a fine powder from an antimony solution and is used as a bronzing pigment for metals and plaster casts.

3. "Antimony vermilion," a red trisulphide of antimony, may be formed by precipitating an antimony salt from solution with sulphureted hydrogen. As a pigment, it is in many ways superior to red oxide of lead, red chromate of lead, or mercury vermilion.

4. "Antimony yellow" is produced by the slow oxidation of the sulphide; various shades of yellow are formed by mixing with red lead and zinc white.

5. "Antimony blue," "antimony violet," etc., are other pigments produced by mixing antimony yellow with other mineral compounds.

Rubber Vulcanizing.—Manufacturers of antimony sulphuret for use in the rubber industry customarily use the words "golden" and "crimson" to indicate pentasulphide and oxysulphide, respectively, and the word "golden-crimson" when both are present. It is still doubtful whether pure pentasulphide as such has ever been prepared. Commercial antimony pentasulphide, or "golden antimony sulphide," is generally supposed to be a mixture of antimony tetrasulphide and free sulphur ($Sb_2S_4 + S$). Whether the "crimson" product is really an oxysulphide of antimony is still doubtful. It has been considered that many of the substances described as oxysulphides of antimony are probably mixtures.

Mordants.—Tartar emetic and antimonine are the principal compounds of antimony that are used as mordants.

Ammunition.—Antimony sulphide in the form of "crudum" is used as a constituent in military and sporting arms primers and as a smoke producer for smoke screens, range-finding shells, and tracer bullets.

Fireproofing.—The largest single use of antimony today is for a new demand, the preparation of an antimony compound with chlorinated rubber or chlorinated paraffin, employing approximately 10,000 tons of the metal per year, for rendering certain essential war fabrics flameproof and fire-resistant. Materials treated with the compound quickly extinguish flames that accompany initial combustion by virtue

of an automatic chemical reaction as the compound itself is heated. Certain new fireproofing pigments of antimony base, employed in ship construction, are also increasing the war consumption.

Other Uses.—In various forms antimony is used in the manufacture of matches, medicine, fireworks, toys, etc.

The Metallurgy of Antimony.—Stibnite, Sb_2S_3 , antimony sulphide, or glance, is the principal ore for the extraction of antimony. The other ores—cervantite, kermesite, valentinite, sernarmonite—are oxide ores and occur sparingly in nature. Dry methods are generally adopted for the extraction of the metal. Electrometallurgical methods have had much attention in America and Germany but have not yet found, on economic grounds, practical or extended application, except in a few rare cases. During recent years, treatment of the poor grades of the ore, especially sulphide ore,

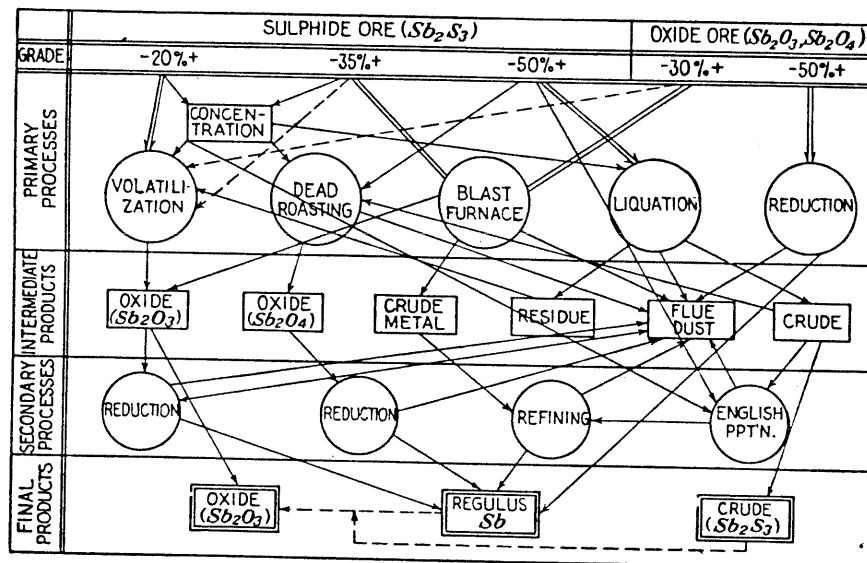


FIG. 1.—Processes for treatment of antimony ore.

by ore-dressing methods has commanded some attention and been adopted in a few cases.

The impure sulphide of antimony, resulting from the liquation process, is called "needle," "liquated," or "crude" antimony, and the refined metal itself is called antimony "regulus."

The accompanying scheme shows the different processes adopted for the treatment of various grades of antimony ores.

Liquation of Crude Antimony.—The first step in the smelting of antimony is a simple one—the process of "liquation," which produces crude or needle antimony. Ores containing about 50 per cent Sb are used in the liquation process for the production of crude. The temperature required for liquation is between 550 and 600°C. Ores to be liquated are broken to about walnut size. If the pieces are larger than this, the low heat used will not penetrate effectively, and if the size is smaller than walnut, the ore tends to pack too closely for adequate penetration. A packed charge also prevents the free escape of the fused sulphide.

Intermittent Liquation in Crucibles.—There has been developed in China a unique type of furnace for crude smelting which, in spite of the heavy loss in antimony

entailed during smelting, is simple in construction and operation, as shown in Fig. 2. The furnace is generally built in four sets of two pots each. The upper pot, which has a $\frac{1}{2}$ -in. hole at the bottom for the liquated product to trickle through, is the container, capable of holding a charge of 45 to 60 catties (1 catty is equivalent to about 1.3 lb.), and the bottom pot, bedded in sand or ashes, is the receiver for the liquated product. Each charge requires 2 to 4 hr. to run, and the life of the pot is generally 10 to 15 days. The liquated product is ladled into a mold, holding 16 lb. of crude. For 60 per cent Sb ore, the extraction is generally 83 per cent of the contained antimony, and for 45 per cent Sb ore, it is as low as about 64 per cent. The residue from the container contains $12\frac{1}{2}$ to 30 per cent Sb, which, as will be seen later, can be extracted in a volatilization furnace.

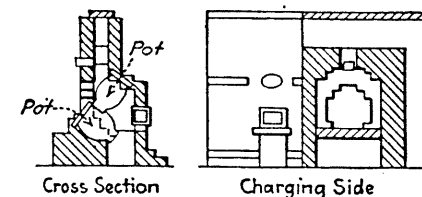


FIG. 2.—Liquation furnace and pots used in China.

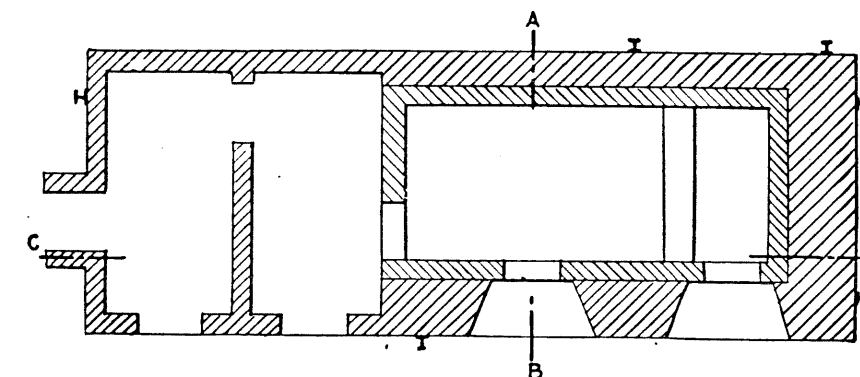
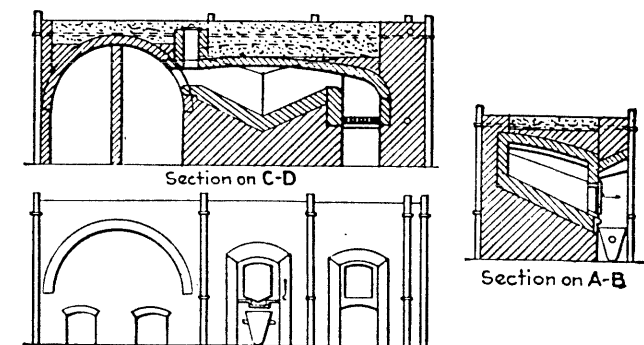


FIG. 3.—Plan of liquating reverberatory furnace.

Continuous Liquation in Reverberatory Furnaces.—The primary object of the liquation process is to free the sulphide of antimony from its associated gangue. As



FIGS. 4-5.—Elevation and cross sections of liquating reverberatory.

carried out in the old-fashioned pots, tubes, or crucibles, it is laborious, expensive, and wasteful. On the other hand, although liquation can be easily carried out in

reverberatory furnaces, the operation is attended with some difficulties. The maintenance of a reducing atmosphere, to prevent the formation of either the volatile trioxide or the stable tetroxide, is not easy to attain. While the trioxide can be partly recovered in any suitable flue or condensation apparatus, the tetroxide, found remaining in the residue, has to be considered as a loss, since it can probably be recovered only in a very high temperature upon further treatment of the residue by the volatilization process. It is regrettable that experimentation with gas-firing has never been tried out, as it is obvious that by such a method of working a reducing atmosphere can be better maintained.

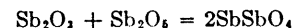
Figures 3 to 5 show the construction of a liquation reverberatory furnace.

The residue from the liquation process, generally retaining about 15 to 25 per cent Sb_2S_3 , may be treated in any of the volatilization furnaces to be described later.

Dead Roasting for the Preparation of the Stable Tetroxide.—Dead roasting as a process is seldom adopted, even with rich sulphide ore or crude, as the intermediate product Sb_2O_3 has no market and has to be finally reduced to the metal. Rich sulphide ores containing about 50 per cent Sb are generally treated by the liquation process for the crude or by the English precipitation method for the metal.

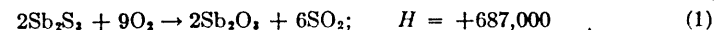
The oxidizing roasting of antimony ore results in either one of two products, depending on the temperature and air control—the volatile trioxide, Sb_2O_3 , or the stable, nonvolatile tetroxide, Sb_2O_4 .

The chemical changes taking place in the production of these two oxides are rather complicated. According to Borchers,¹ the tetroxide, Sb_2O_4 , which he regarded as a salt resulting from the reaction of the pentoxide, Sb_2O_5 , having an acidic character, with the trioxide, Sb_2O_3 , having a basic character, is thus produced:



However, from a study of the temperature control of the roasting of the sulphide for the derivation of the various oxides, the authors now consider the above reaction to be apart from the facts. In a general way, when the sulphide, Sb_2S_3 , is roasted, the following chemical changes take place:

Below 500°C.



Between 500 and 900°C.



In other words, the tetroxide is derived directly from the trioxide and is not formed by the mutual reaction of the trioxide with the pentoxide. When the sulphide is heated below the temperature indicated in formula (1), the trioxide is formed with evolution of heat, amounting to 687,000 cal. This heat would instantaneously bring the particles of nascent Sb_2O_3 to temperatures well above 500°C. which then renders the reaction according to formula (2) possible, if an excess of oxygen is present.

When oxides of other metals are present, antimonates are formed. If, also, sulphides of foreign metals are associated with the stibnite, these foreign metals are brought mostly to the form of antimonates, instead of remaining, as they would under ordinary circumstances, as sulphates. If the proper temperature (below 500°C.) and an excess of air have been maintained, and if, in the case of rich ores, constant rabbling has been performed, the roasted mass should contain the tetroxide principally. Under ordinary working conditions, however, the product will contain antimony glass, undecomposed stibnite, and antimonates, arsenates, and sulphates of the foreign metals present. Much attention must be paid to the regular rabbling

¹ Zinn, Wismut, Antimon, "Metallhüttenbetriebe," Vol. 4, p. 138, W. Knapp, Halle, 1924.

of the charge as the richer parts of the ore tend to liquefy and to frit together. The richer the ore, the more difficult it is to roast. Toward the end of the roasting, the temperature should be raised a little, in order to complete the oxidation of any undecomposed sulphide. If carried at too high a temperature, however, the mass will frit together, and the penetration of air to the interior is prevented, and both the sulphide and oxide are volatilized.

A charge properly roasted has a reddish color while in the furnace and an ashy-gray color on cooling, and there should be no evidence of fritting in the furnace. If

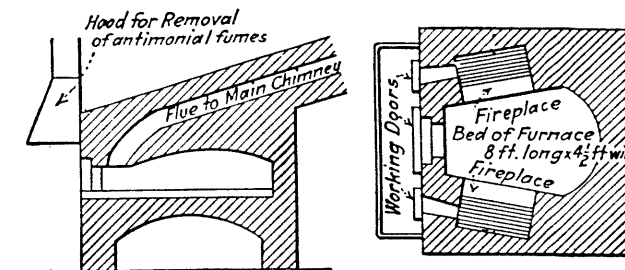


FIG. 6.—Long-bedded reverberatory.

an excess of air has not been available, the roasted product will be largely the volatile trioxide instead of the tetroxide.

The roasting of stibnite for the production of tetroxide is generally carried out in reverberatory furnaces provided with condensing apparatus. The furnaces are of two kinds: (1) small rabble furnaces (egg-shaped hearth), (2) long-bed reverberatory furnaces (similar to the hand-reverberatories of lead smelting practice). Figure 6 shows the small-type rabble furnace used in France.

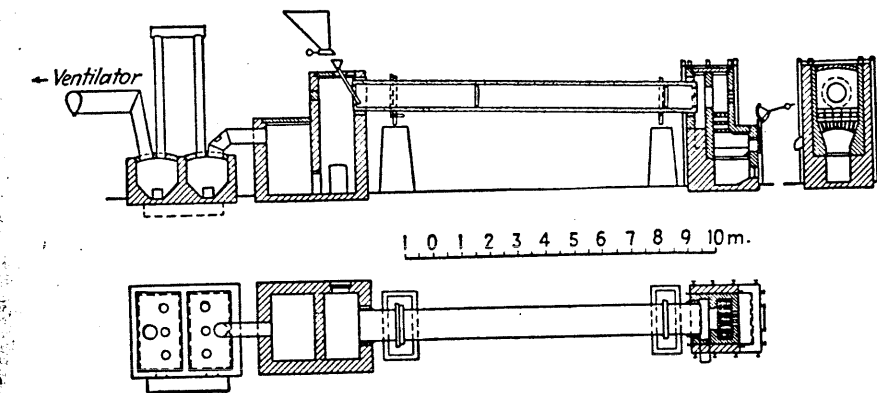


FIG. 7.—Cylindrical roasting furnace.

A rabble furnace of this type handles a charge of 5 to 6 cwt. of ground and screened ore in about 6 hr. The time required varies from 3 to 12 hr., according to the richness of the ore. During the first 2 hr. the door must be closed, but toward the end it is opened for stirring and rabbling the charge and for free admission of an excess of air. Loss of antimony in this furnace treatment varies from 4 to 8 per cent.

The long-bedded reverberatory of German, French, Italian, and American plants is about 40 ft. long by 76 in. wide. It has 8 or 10 working doors on each side and car-

ries about $1\frac{1}{2}$ tons of ore, of which 6 cwt. are charged at a time. The ore works through the furnace in about 40 hr.; during the last 2 hr. before drawing, the charge is thoroughly rabbled every 5 min. and the heat is strong. Properly roasted ore has a dull grayish-yellow color. Loss of antimony in these long-hearth furnaces runs about 8 per cent.

Furnaces with a trough-shaped hearth, sloping toward one side, have been proposed, but are not in successful use, for the carrying on of both reduction and roasting at the same time. The slope of the hearth is for tapping out any accumulation of sulphide that liquates during the roasting.

The dead roasting of the ore or of the crude as carried out in reverberatory furnaces is simple, but is not entirely satisfactory, as constant and vigilant attention is required to prevent the fritting of the mass, which, when once formed, would prevent the penetration of the air to oxidize the interior of the mass. To obviate such diffi-

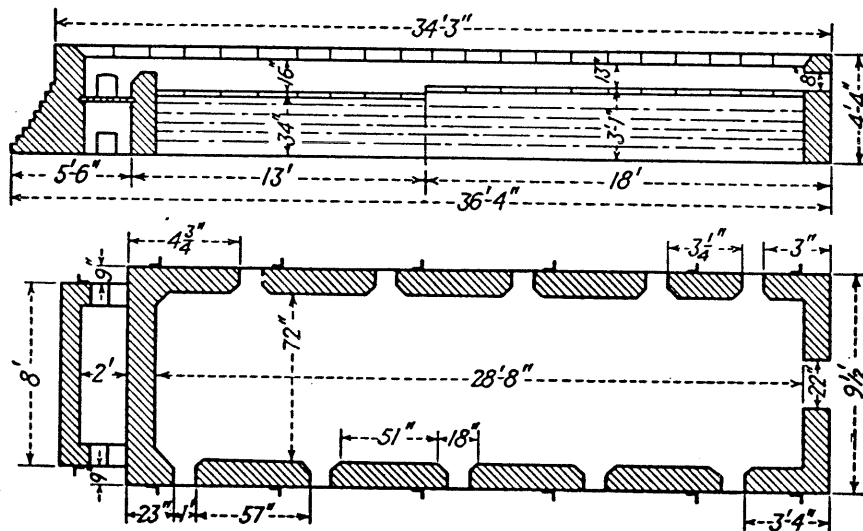


Fig. 8.—Reverberatory roasting furnace.

culty as well as efficiently to oxidize the charge to the stable tetroxide without the expenditure of much labor, A. Lissner and E. Eichelter¹ have made use of a cylindrical rotary furnace of 12 to 20 m. in length, with some degree of success, as illustrated in Fig. 7. Such a furnace can be fired with flaming coal or gas, preferably with the latter. The draught can be regulated with a ventilator, while any volatile oxide formed can be condensed in any suitable flue or condensation apparatus.

At the Wah Chang Mining & Smelting Co., Changsha, China, the crude was first ground into powder in a Chilean mill and was then fed into a reverberatory furnace, as shown in Fig. 8, which could dead-roast 2000 lb. (906 kg.) of crude per 24 hr. with a consumption of 700 lb. (317 kg.) of coal. Two workmen were required per furnace per shift of 12 hr.

Volatilization Roasting for the Trioxide.—Practically all the shaft furnaces for the volatilization process are based on the same principle. The ideal ore for treatment

¹The Use of a Rotary Furnace for the Roasting of Rich Antimony Ore, *Metall u. Erz.*, Vol. 19, p. 373, 1922.

in such furnaces is one containing 15 to 25 per cent antimony; ore above 40 per cent Sb would partly volatilize and partly liquate, and part of the liquated product would combine with the volatilized trioxide to form an oxysulphide compound, commonly known as "antimony glass," which causes fritting at the lower zone of the furnace. Even with ore containing 30 to 35 per cent Sb, some fritting might occur, necessitating the maintenance of the furnace at a higher temperature than necessary for poorer ores. Hence the paradox: the richer the ore, the higher the percentage of coke required for the charge. It is possible to volatilize an ore of about 20 per cent with 4 to 6 per cent charcoal, the temperature being thus kept at low red-heat. On the other hand, with liquation residue which ranges from 15 to 25 per cent, the problem is different. Here we have a material that disintegrates and packs at a very low red heat, thus partially blocking up the furnace and preventing free passage of the air upward. To remedy this, some works use a forced draft, while others use an excess of coke, amounting to 30 to 50 per cent of the charge, thus increasing the porosity of the charge. One can frequently tell when the furnace is blocked or when the suction fan is choked with the trioxide, especially if water is introduced into it, by observing the appearance of a reddish tint in the issuing trioxide fume, which would be white with the furnace working under normal conditions. A plausible explanation for the appearance of this reddish tint in the otherwise white trioxide is found in the formation of the compounds $Sb_2S_3 \cdot O$, $Sb_2O_3 \cdot 2Sb_2S_3$, $Sb_2O_3 \cdot 2Sb_2S_3 \cdot 4H_2O$, or $Sb_2S_3 \cdot 2H_2O$. Some sulphide particles from lack of free oxygen might be volatilized as such at temperatures above $650^\circ C.$, taking up the moisture still in the ore. Another fact, which seems to substantiate such an explanation, is that whenever a new furnace, or one that has been standing idle for some time, is started the trioxide fume is frequently colored red at the commencement and continues so until the furnace is well under way. The explanation here is that there must be present a certain amount of moisture in the furnace, and it is this moisture that is taken up by the volatilized sulphide to form the above-mentioned red hydrated sulphide. In fact, an analysis of this pinkish oxide sometimes shows the presence of 5 to 6 per cent S.

It is impossible to maintain uniform temperatures throughout the furnace shaft. The bottom part of the furnace, where the burned-out ore is ready to discharge, is cooled by the incoming air, while the top part is also comparatively cool. The central part thus localizes a hot zone of reaction where fusion of the silicate-forming minerals of the gangue and in the coke causes frequent trouble.

While Otto Barth¹ states that the volatile trioxide exists only below 700° and above 1100° , our experience indicates that antimony sulphide, when roasted under properly restricted admission of air, changes to the volatile trioxide below 445 or 560° and above 930° , while between the two limits, the oxide exists only as the stable tetroxide. In practice, the stable tetroxide may be considered to exist between 500 and 1000° . It is thus obvious that proper control of temperature is important for the successful operation of the volatilization process.

The many advantages of this method of treating low-grade antimony ores have brought it into general favor, and it is extensively used in one form or another in France, China, Yugoslavia, and elsewhere. These advantages are: (1) When the ores contain precious metals these are found in the residues after volatilization. (2) Barring dressing the ores, it is the only method really suited to low-grade ores. (3) With different devices for condensation, the loss of antimony can be greatly lessened. (4) Less fuel is required, as the sulphur in the ore can be utilized as fuel. (5) The condensed trioxide can be reduced to metallic antimony, or it can be marketed as white oxide to make paint, enamels, etc.

¹"Die Metallverfluchtungsverfahren mit besonderer Berücksichtigung der Herstellung von Zinkoxyd," p. 65, W. Knapp, Halle, 1935.

Of the various modifications that have been developed in the volatilization method of producing antimony trioxide, the following important ones are described.

Herrenschmidt Process.—Figure 9b is a longitudinal section and view of Herrenschmidt's finally perfected equipment (1908). Figure 9a is a cross section of a roasting furnace along AB. Figure 9c is a longitudinal section along JY.

The broken ore, carrying 10 to 20 per cent antimony, is charged, mixed with 4 to 8 per cent charcoal, into the roasting furnace *a* the bottom of which is formed by horizontal iron bars *b*. The volatile antimony trioxide is deposited on condensation pipes *e*, in the condensing chambers *d*, under suction from the two fans *h*. The last trace of the uncondensed oxide is caught by the water coming from the coke tower *i*, at the top of which are the water pipe *j* and the seesaw water distributor *k*. The roasting furnace is built partly of bricks, partly of cast metal. The condensing chambers are of cast iron, and the coke tower of wood. Each condensing chamber is 1 m. long.

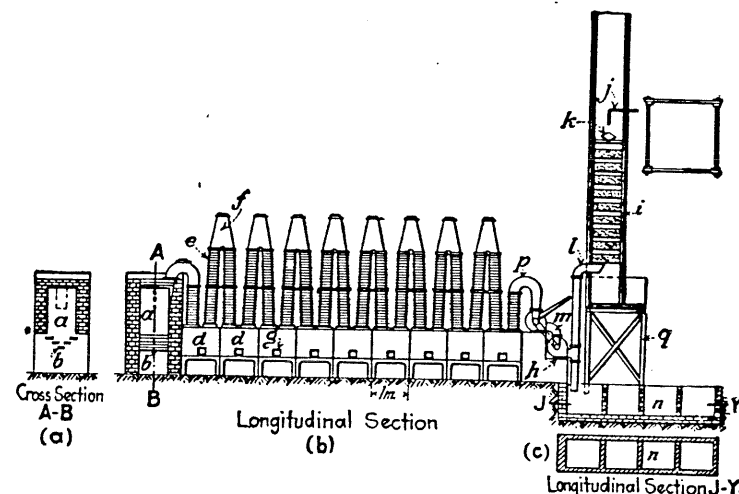


FIG. 9.—Perfected Herrenschmidt volatilization and condensation apparatus.

With mine-run ores, carrying 10 to 15 per cent antimony, 6 tons can be treated in 24 hr., with a fuel consumption of 4 to 5 per cent gas coke or 6 to 7 per cent charcoal. With ore containing 18 to 20 per cent antimony, $4\frac{1}{2}$ tons per 24 hr. can be treated with a fuel burden of 5 to 6 per cent gas coke or 7 to 8 per cent charcoal. Each unit employs four workmen per 24 hr., and the fans and pump require 3 hp.

Gas coke gives better results, if obtainable, but most of this antimony work is done in out-of-the-way places, where charcoal is cheaper.

The size of the ore treated is 1 to 4 cm. Ore dust must be separated out, and, if present in large quantity, must be briquetted with 7 or 8 per cent clay into balls of proper size and charged along with the ore. The working of the furnace proceeds as follows:

A charge of old scoria is placed on the grates up to a height of about 10 cm. above the uppermost bar; and wood and charcoal are put in to a height of another 10 cm. As soon as the fuel is lighted and burning freely, another charge of 300 kg. of scoria, mixed with 6 per cent charcoal, is put in. Finally, when the furnace is up almost to full heat, an ore charge of 50 kg., mixed with 2 kg. of charcoal, is put in, and this is continued until the furnace is full to within 30 cm. from the mouth. The same charge

is repeated every 12 to 14 min., according to the rate of revolution of the ventilating fans—which is 1200 to 1400 r.p.m.—and the scoria is discharged accordingly.

The temperature of roasting, for trioxide production, should not be over 500°C. About 30 cu. m. of water per day are required for one apparatus.

The loss of antimony in the Herrenschmidt apparatus is variable, approximating 10 per cent; the skill of the laborer is all-important. By manipulation and spreading of ore and fuel so that the ore is thoroughly burned and the antimony contents fully volatilized, the percentage of fuel can at times be cut down to about 3 per cent, and the yield of oxide can be increased to 95 per cent.

The Wah Chang Mining & Smelting Co.'s plants in China, for several years the leading producers of antimony, used about 15 per cent charcoal on ore running 20 to 35 per cent antimony; if the charge consisted of liquation residue, the charcoal required amounted to 20 to 22 per cent for coarse and 24 per cent for fine. The scoria discharged from the shaft furnaces generally carried about 3.5 per cent antimony from ore charges, and 4.5 per cent antimony from the liquation residue charge.

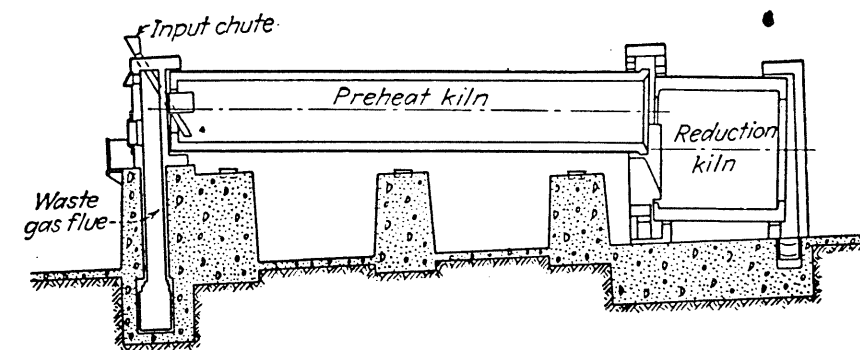


FIG. 10.—The Follisain furnace.

The Follisain Furnace.¹—In 1926, Friedr. Krupp-Grusonwerk A. G. patented the so-called Waelz process for the treatment of zinc, lead, cadmium, arsenic, antimony, bismuth, and tin ores. This process has been adopted by the Podringi Consolidated Mines Ltd., in their antimony smelting work at Krupanj, Yugoslavia. In principle, the Waelz process is somewhat similar to the Follisain process.

The Follisain furnace as illustrated by the diagrammatic drawing (Fig. 10) is a revolving furnace. The preheating kiln is approximately 30 ft. long and 36 in. internal diameter, and the secondary or carbon combustion zone is about 7 or 8 ft. long by 6 or 7 ft. diameter. The air for combustion is heated in an air heater to about 750°C. The waste gases carrying the antimony trioxide fume leave the kiln at a temperature of 230 to 250°C. and are then passed to a Cottrell electric precipitation plant for the recovery of the antimony trioxide. Fuel consumption is 25 to 30 per cent of the weight of ore charged. Power consumption is $5\frac{1}{2}$ to 6 kw.-hr. per ton of ore treated. For the treatment of, say, 20 tons of 20 per cent Sb ore per day, two revolving furnaces, as illustrated, are required.

Antimony Smelting at Cortis Rosas (Ballao), Sardinia.²—It is interesting to note that in this smelter a converter has been adopted for the volatilization process. It seems that this converter is an adoption of the "convertisseur" apparatus patented

¹ Private information from Follisain Syndicate Ltd. (London).

² Sul trattamento dei minerali di antimonio in Sardegna, *Industria*, Vol. 32, pp. 437-438, July 31, 1918.

by Collin¹ in France. The converter is composed of two parts, as shown in Fig. 11; the bottom part, which is hemispherical in shape and can be revolved horizontally on two bearings for the discharging of its contents, and the top part, which acts as a hood. Compressed air enters from the bottom, while the volatile fume is drawn from the top of the hood by means of an aspirator. This method is specially adaptable to the treatment of fine ore, especially ore of a calcareous nature, which if treated in a shaft furnace, would render the operation difficult and troublesome.

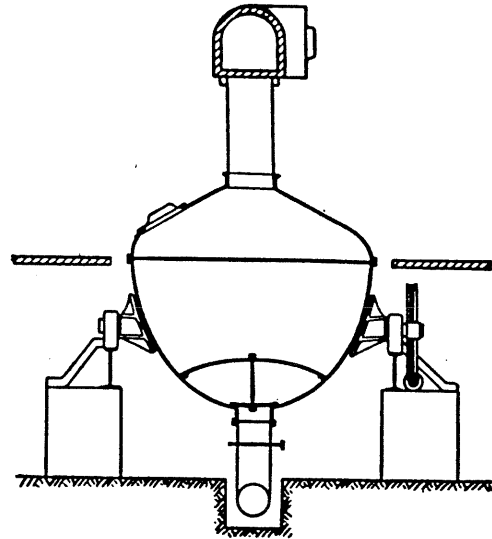


FIG. 11.—Cortis Rosas converter.

The Blast Roaster.²—The blast roaster as shown in Fig. 12 is intended to be an improvement of the usual shaft furnace for treating low-grade antimony ores. It is in principle a modified form of water-seal gas producer, employing mechanical charging and discharging devices. The blower delivers air to an annular space or wind box around the furnace, before entering the latter through the grate. The coke consumption for the roasting proper will be lower than that for an ordinary shaft furnace, as the air is preheated.

The blast roaster differs from the ordinary shaft roasting furnace mainly in that it uses air under pressure instead of under suction. Since the product of roasting is volatile antimony trioxide, it is obvious that an upward movement of air under pressure through the ore bed would be more positive in assisting volatilization of the trioxide besides furnishing the necessary oxygen for chemical reactions. It also uses a principle of blast roasting in its progressive roasting action through the ore bed, but it differs from the general practice of blast roasting in that the sulphur content of the whole charge is low, only about 7.17 per cent (assuming 20 per cent Sb ore grade and 10 per cent coke consumption) as against 12 to 14 per cent for lead and zinc ores in blast roasting; therefore there will be no incipient fusion of the ore particles, which is an essential factor of the latter process. Although it is like a gas producer in both

¹ Convertisseur pour la séparation des métaux fixes et volatils dans les minéraux complexes, Marcel Collin, French patent 428708, Sept. 6, 1911.

² Private communication from C. C. Chao, metallurgist of the National Resources Commission, China.

construction and operation, there will be no reducing effect because (1) the coke in the charge is isolated by the excessive gangue of ore and (2) the blast delivered will be more than sufficient for the theoretical roasting and combustion, thus ensuring an oxidizing atmosphere throughout the ore column. It also differs from the blast-furnace smelting in not slagging the gangue with fluxes and in treating a low grade of ore. Thus there will be no self-reduction effect of stibnite.

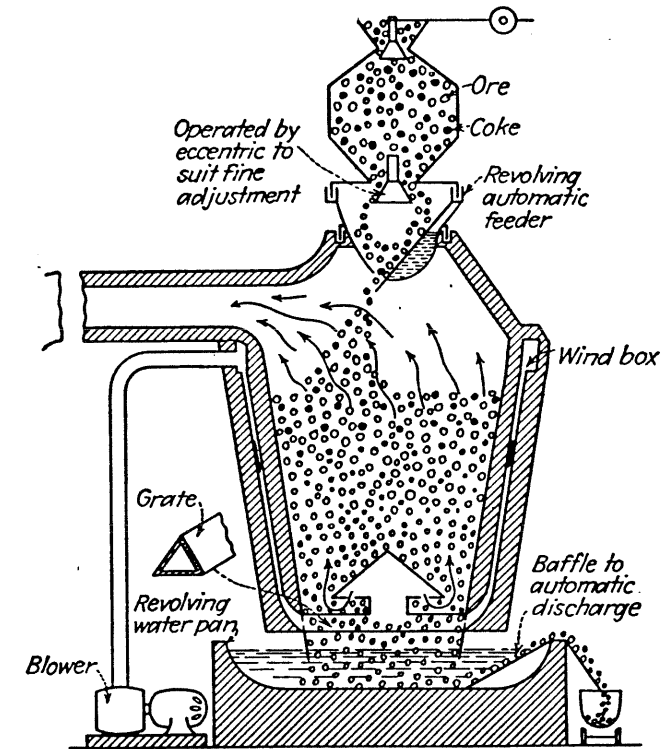


FIG. 12.—Blast roaster.

Other Processes for Preparation of the Trioxide.—There are perhaps a dozen processes for the preparation of the volatile trioxide, which at different periods, in France, Italy, and Germany, have had some prestige. In all of them, the principle of roasting, volatilizing, and condensation of the oxide is, of course, the same; differences exist merely in the forms of furnaces, condensers, and methods of collecting the oxide.

In the Chatillon process, which has been employed on a large scale in France, the furnace consists of two double cupolas terminating in a common flue from which the volatilized oxides are led to water-cooled condensing chambers made of sheet iron. The upper cupolas are charged with alternate layers of fuel and ore, and as the liquated sulphide melts and falls through to the lower cupola, it meets an upward current of hot air that converts it into the trioxide, Sb_2O_3 . Before leaving the plant the gases are reduced to a temperature of 100°C. and passed through a baghouse. The sublimate obtained contains 98 to 99 per cent antimony trioxide.

The Blast Furnace.—The blast furnace can be operated as a producer of both antimony trioxide and metal at the same time. Treatment of this subject will be taken up under the next heading.

Pigment Trioxide.—The trioxide, as produced in the treatment of the ore by the volatilization process, is generally impure and coarse and hence is not suitable for pigment purposes, although it may be used as an opacifying agent for white enamels.

The following processes may be adopted for the production of pigment trioxide.

The process adopted by the antimony smelter at Costerfield, Victoria, Australia, was as follows:¹ "The furnace was a small circular cupola with four tuyères at the top of the hearth and two more admitting air to the top of the charge above the feed door. The condensing section of this plant consisted of a firebrick and red brick chamber, a cyclone, and baghouse with a centrifugal fan placed in the circuit at the intake of the baghouse. The oxide with a small amount of reduction slag from the starting furnace was charged into the furnace on a bed of burning coke where it soon volatilized. The cooling of this oxide took place very rapidly so that it was deposited mostly in the amorphous form as very small spheres. A small amount of crystalline oxide was also collected at the cyclone. The baghouse product was the most suitable as a pigment on account of the fine state of division of the particles, approximately 0.0025 mm. in diameter, and its spherical form and whiteness."

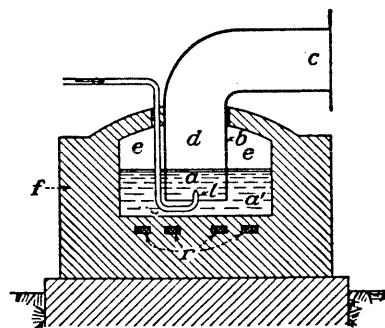


FIG. 13.—Germot trioxide furnace.

resistances r , receives an inverted bell b , provided with one or more blowing-in tubes l , which open at the lower part of the furnace, the orifices of the tubes being disposed above the lower edge of the bell. The bell b , dipping into the metallic bath a , thus forms a closed chamber d which contains only the air or oxygen blown in by tubes l . The air oxidizes the molten metallic antimony to Sb_2O_3 in the state of clouds of impalpable powder, which is discharged through the neck c and collects in any settling chambers. Fresh antimony in lumps is added to the bath from time to time.

Jean Joseph Listrat² proposes to treat antimony sulphide ore, for liquation and volatilization as antimony trioxide, in one operation. However, it has been found in practice that antimony crude alone forms the best charge for such treatment. The apparatus consists of a furnace 10 (Fig. 14) having three cupola chambers 11, 12, and 13. The central chamber 12 communicates with any receiving apparatus for the fumes of oxide given off, and the end chambers 11 and 13 are directly connected to any condensation apparatus. Air is blown into these chambers through inclined pipes 14. Antimony ore or antimony sulphide is introduced into the central cupola chamber 12. Any suitable source of external heat is used for originally heating the central chamber after which, when the process gets under way, the exothermic reactions will provide all the necessary heat. The gangue from the ore charged may be taken off at proper intervals through the taphole. The purest oxide obtained is from chambers 11 and 13.

¹ McLEAN, *Chem. Eng. Mining Rev.*, Dec. 6, 1926, pp. 94-95.

² British patent 203519 (1922); U. S. patent, 1504685, Aug. 12, 1924.

³ U. S. patent 1873774, Aug. 23, 1932.

Antimony oxide pigment,¹ known in England under the trade name Timonox, is now manufactured in France by a patented process,² by which metallic antimony obtained by dissociating the trisulphide at a high temperature, probably above 1020°C., is subsequently oxidized to the trioxide. Traces of sulphur trioxide in the antimony oxide are removed by vigorous washing in lime water, agitated by compressed air.

The main points of the process³ as patented by the Deutsche Schmelz-u.-Raffinerwerke A. G. for the manufacture of antimony oxide for pigment purposes are: (1) the air for oxidizing the metal is diluted by nitrogen, carbon dioxide, combustion gases, principally by exhaust gases; (2) the antimony used is directly heated by burning gas which plays on the surface of the metal; (3) the oxygen content of the flame is so adjusted that the antimony oxide obtained is amorphous; (4) the temperature of the antimony bath must be brought to about 1000°C.

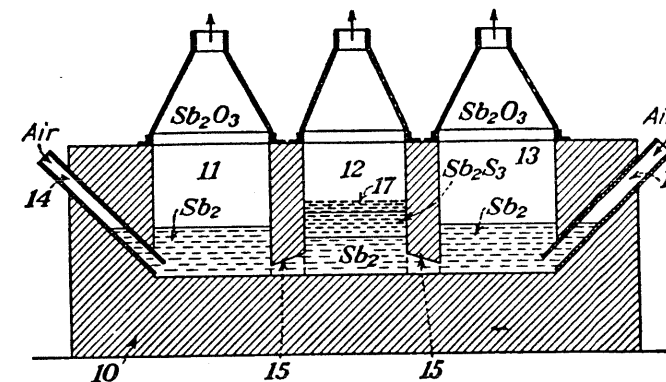


FIG. 14.—Listrat antimony furnace.

Methods for the Production of Metallic Antimony.—The last phase in the metallurgy of antimony is the production and refining of metallic antimony. Unrefined antimony metal is sometimes called crude antimony, but the metal is never marketed in this form; the name would be confused with liquated sulphide which is commonly called crude antimony, or more correctly antimony *crudum*. Antimony metal may be obtained from (1) the oxides (trioxide or tetroxide), (2) from antimony *crudum*, or (3) by direct smelting of antimony ores. Of these methods, the bulk of the world's antimony, up to the present time, has been produced by the first two mentioned.

The direct smelting of metal from its ores was receiving a great deal of attention, however, in the United States (San Pedro), Mexico (Wadley), and England during the period just preceding 1918, and in earlier years at Banya in Bohemia, and some very successful results were being achieved. It is not overstating the case to say that the operators of the blast furnaces engaged in this direct smelting had, prior to the great metal depression, already accomplished such progress in the normal blast-furnace reduction of antimony ores as to indicate the possibility of a complete reconstruction of the practice of antimony metallurgy. In fact, at the present time, at the Laredo plant in Texas, at a plant near Mexico City, Mexico, and at a plant in France, blast-furnace practice is adopted. It is well demonstrated that the blast furnace is the best appliance for a certain class of antimony ores—those containing

¹ *Chem. Trade Jour.*, Vol. 83, pp. 337-338, 363-364, Oct. 19, 26, 1928.

² *Metal u. Erz.*, Vol. 29, pp. 105-113, March, 1932.

³ British patent 345034, Mar. 19, 1931.

The singles are next purified by fusion with a small amount of liquated sulphide of antimony, to remove the iron remaining in the metal. The charge for this second, or "doubling," process is: singles (broken small), 84 lb.; antimony crude, 7 lb.; salt, 4 lb.

The fused mass is stirred occasionally with an iron rod, the time required for one charge being about 1½ hr. When fusion is complete, the slag and matte are ladled off with an iron spoon and the contents of the crucible poured into the molds used in the previous fusion; the matte and skimmings are added to subsequent ore smeltings. The metal thus obtained is known as "star bowls," and contains 99.0 to 99.53 per cent antimony, 0.18 per cent iron, and 0.16 per cent sulphur.¹

The effectiveness of this second liquation can be understood when it is remembered that in such an alloy of antimony and iron intermetallic compounds are present. One of these, with the chemical formula Fe_3Sb_2 , has a freezing point of 1016°C., and another ($FeSb_2$), which forms from Fe_2Sb_2 and liquid, crystallizes out at 730°C. The melting point of pure antimony is 630°C. Hence, in the heating up of this alloy, the antimony first melts and the antimony-iron compounds tend to separate and rise to the surface. These are then "taken up" by the slag and removed from the bath of metal under purification.

The presence of sulphur, due to the excess of crude used, is indicated by the crystalline pattern that forms on the surface of the metal being covered with small glistening patches, the latter being known as "flouring." In order to remove this sulphur, another fusion is necessary.

Starring.—The custom of the trade is to demand antimony that is "starred," or crystallized, on the upper surface, and it is at this stage that this "star" is obtained. These two results are accomplished by melting the metal with what is known as the "antimony flux," a substance that is often difficult to obtain, in proper composition, at first. This flux is prepared by rule-of-thumb method, about as follows: 3 parts of ordinary potash are melted in a crucible, and 2 parts of ground liquated sulphide are mixed in. When fusion has become quiet, the mixture is poured out and tried on a small scale to find out whether it yields a good star. If the star is satisfactory, the ingot of metal obtained is then broken and the metal examined in order to determine whether it is free from sulphur. If, however, a good star is not obtained, the flux is remelted, and more of one ingredient or the other is added as experience dictates.

The first of these operations of the precipitation process—smelting the crude with iron—is called "singling," the second operation—resmelting the singles for the production of the bowl metal—is called "doubling," and the last operation is called "refining," or "frenching."

Direct Extraction of Metal from Ore or Crude.—(Reverberatory Bath Furnaces). Several patents have been taken out (Sanderson, Cookson, Herrenschildt) on the direct smelting of antimony sulphide in a bath of ferrous sulphide, on the hearth of a reverberatory furnace. This method has given good results but has had no wide adoption commercially. After the hot ore has been charged into the reverberatory and thoroughly rabbled, iron is added together with a certain amount of soda ash, the temperature raised, and, when decomposition of stibnite by iron is complete, the antimony metal is tapped. The taphole is closed as soon as the iron sulphide appears. Slag is drawn through the working doors, and as the iron sulphide increases during the operation it is removed until the bath is reduced to its original depth.

At a smelter in Mayenne, France,² using a reverberatory furnace with a bed 10 ft. long by 4 ft. wide, the charge made up every 3 hr. was as follows:

¹ In Japan at the Saijo Smeltery, the Star Bowl metal carried 97 to 98 per cent Sb, 1.5 per cent Fe, and 0.7 to 0.8 per cent S.

² GOWLAND, "The Metallurgy of Non-ferrous Metals," revised by C. D. Bannister, 4th ed., 1936, pp. 570-575.

	Pounds
Rich ore (50 to 60 per cent Sb).....	992
Worked ore fines (about 45 per cent Sb).....	330
Slag from second or refining fusion (about 20 per cent Sb).....	44
Sodium carbonate.....	44
Scrap iron.....	529

At the Wilhelmsberg Works, in Germany, reverberatory furnaces fired with gas were adopted for the smelting of the crude. The first smelting was done in a furnace having an elliptical hearth whose area was 300 × 500 cm. The charge was made up of 3000 kg. of crude and 1000 to 2000 kg. of iron, soda, salt, slag, and charcoal or anthracite. The use of powdered charcoal or anthracite was to prevent the excessive loss of antimony due to volatilization. The time required for the smelting was 5 to 6 hr., and the consumption of coal was 525 kg. per ton of the crude charged. The crude metal contained on an average 3.5 per cent Fe. The average result was Sb in the raw metal, 86 to 88 per cent; Sb in the slag, 8 to 10 per cent; loss due to volatilization, 4 to 6 per cent. This metal was refined in another reverberatory furnace, having a hearth area of 150 × 250 cm. The charge was made up of 1500 kg. of raw metal, plus soda, charcoal or anthracite, old refinery slag or couverture slag. Time required was ½ to ¾ hr., and the coal required was 400 kg. per ton of regulus produced. Average loss was 6.5 per cent, counting the antimony content of metal in the raw metal as well as that of the slag and couverture charged.

Water-jacket Blast-furnace Smelting.—The blast-furnace smelting of antimony ores, both sulphide and oxide, is entirely feasible and will undoubtedly come into more common use as the industry advances. Already, in Mexico, California, and England, successful blast-furnace smelting has been under way for several years, proceeding along lines only slightly modified from regular lead-smelting practice.

The operators of these blast-furnace plants are most enthusiastic regarding the advantages and ultimate general adoption of this method, asserting confidently that the first page of antimony metallurgy has hardly been written and that the blast-furnace process will extensively replace the old existing methods in the industry. That this may come about in Europe, Mexico, and America there is little question. Under existing ownerships and conditions in China, however, it is extremely improbable that any reshaping of the industry will take place.

Attempts to smelt unroasted stibnite ores in water-jacketed blast furnaces did not come to any successful result until recent years, and published information on the subject is exceedingly meager. There is a marked difference in the behavior of stibnite and that of other metallic sulphides in the blast furnace. It has been found best to add no metallic iron to the charge and to regulate the coke so as to preclude any reduction of ferrous oxide in the flux. No iron available for matte is provided, and matte is usually absent. Any addition, or presence, of metallic iron will always result in the production of an antimony-iron alloy—speiss.

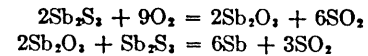
It is usually found that the contents of the furnace crucible gradually freeze from the bottom upward, and the entire crucible is eventually a solid mass. It is frequently the practice to fill the crucible with firebrick and separate the mixed flow of slag and metal in a shallow reverberatory forehearth.

While the blast-furnace smelting of stibnite has not enjoyed the long industrial history of the volatilization and English precipitation methods, it is to be stated that the best conditions for the process appear to be less than 10 per cent of coke, low blast pressure, low metal content of the charge (about 10 per cent), high smelting column (over 15 ft.), and separation of slag and metal in a heated forehearth. In an efficient plant, the great bulk of the volatilized material is recovered in baghouses, but it is, of

course, undesirable to have to re-treat a large amount of fine material unsuitable for blast-furnace work. The flue dust is best treated in a reverberatory, while the fume is useful in refining, or it may be used as raw material for the manufacture of antimony compounds.

The blast-furnace process does not appear to be adapted for the treatment of high-grade stibnite ore. Loss by volatilization is common to all forms of antimony smelting, and in this respect the blast furnace is far worse than the reverberatory, where a layer of flux or slag protects the metal. With low-grade material, however, which it is difficult or wasteful to treat by other methods, the blast furnace offers decided advantages, *i.e.*, where large quantities of poor ores, fowl slags, mattes, or liquation residues have to be worked up. It is a favored mode of smelting for all materials containing about 25 to 40 per cent antimony, which can be mixed with fluxes to give a charge sufficiently poor in metal to hold down volatilization.

It is pointed out by Schoeller¹ that the production of antimony from stibnite in the blast furnace is an oxidizing process in which the metal is formed in two stages that proceed simultaneously; (1) the molten stibnite absorbs oxygen from the blast; (2) the oxide at once reacts with the unaltered sulphide (roast-reaction process) to form metal and sulphur dioxide, thus:



In endorsing this theory of the blast-furnace process, it is realized that it has been a commonly held belief that antimony sulphide and trioxide do not react on each other as do the corresponding lead and copper compounds, but that the antimony compounds fuse together to an antimony glass. The latter reaction occurs, without question, if the oxide-sulphide mixture is fused in a crucible under a layer of salt, but if stibnite is roasted with insufficient access of air, some oxide will be formed which will react with the unaltered sulphide, part of the antimony settling out in a metallic state. The roast-reaction process does, therefore, have a part in the smelting of antimony. It appears, in some degree as well, in the process of liquation, the metallurgical operation carried on on a large scale in China, for the concentration by fire of antimony-sulphide ores. Examination of this crude discloses the fact that it is not pure antimony sulphide, but a complex solid solution, containing oxide and free metal. The molten sulphide in trickling down from the upper pot absorbs oxygen from the air rising from the crude already collected, which partly converts it to trioxide. This reacts with more sulphide to form metal and SO_2 , which latter is carried away by the draft, allowing the reaction to proceed. Once the material has collected in the lower pot, the reaction is arrested on account of the lower temperature and the small surface exposed. It is thus proved that molten antimony sulphide by itself, in an air current, is partly converted into antimony, and the product also contains the trioxide.

The Mace Blast Furnace.²—The Mace blast furnace is a distinct improvement on the usual type of blast furnace for antimony smelting. The main variations from the old type blast furnace are (1) diametrically opposed rectangular tuyères below the shaft of the furnace in place of the circular tuyères spaced at regular intervals in the lower part of the water jackets, and (2) a removable crucible in place of a solid crucible built on the ground. There are several advantages in the use of the rectangular tuyères which extend the full length of the furnace on both sides. The

¹ Blast-furnace Smelting of Stibnite with Consideration on the Metallurgy of Antimony, *Trans. Inst. Mining Met. (London)*, Vol. 27, pp. 237-267, 1917-1918.

² Private communication from H. C. Mace.

whole hearth area is active, and the dead spaces that exist between the tuyères of the older type furnaces are eliminated. This gives a uniform and intense combustion over the entire hearth.

On account of the open tuyère, the Mace furnace uses lower blast pressure (as low as 4 oz. per sq. in.) which is an important feature in continuous operation of the smaller units. The tuyères are so constructed that the opening into the furnace hearth can be adjusted. For oxidization and volatilization smelting, the slot is left wide open so that a large volume of air under low pressure can be admitted. For reduction smelting, the slot is narrowed. Another advantage of the open tuyère is that any accretions can be removed from the furnace by drawing them into the wind box with the hook instead of punching the dead material back into the furnace as is necessary with the circular tuyères. The advantages of the removable crucible are evident.

The antimony plant set up recently near Mexico City, Mexico, has a Mace furnace in operation. The ore treated is an oxide ore, containing a small amount of stibnite, having the following composition: Sb, 36.0; SiO_2 , 48.0; S, 5.0; Fe, 1.05; Al_2O_3 , 0.6; CaO, 2.0; MgO, 1.4 per cent.

The gangue is principally silica, running from 45 to 52 per cent, and the antimony runs from 35 to 38 per cent. Limestone and hematite are used for flux in the blast furnace to slag the silica, and the furnace charge is about 50 per cent ore and 50 per cent flux with 15 per cent of the weight of the charge coke. The furnace is run with a low column and a hot top to volatilize the maximum amount of the antimony. A small amount of antimony single metal, assaying 91 per cent antimony and 9 per cent iron, is produced, but no matte. The baghouse oxide assays 81.6 per cent antimony, and apparently the only impurity in it is a small amount of carbon dust from the coke. The baghouse oxide is mixed with 15 per cent fine charcoal and 6 per cent soda ash and is reduced in a reverberatory furnace to metal. The capacity of the furnace is 30 tons of charge in 24 hr.

Blast-furnace Smelting for Antimonial Lead.—The International Lead Refining Co.¹ treated antimony sulphide ore (25 to 60 per cent Sb, 6 to 45 per cent SiO_2) and antimony oxide ore (20 to 40 per cent Sb, 10 to 45 per cent SiO_2) in a blast furnace, in which were added the secondary materials, such as battery plates, battery mud, lead oxide, paint and other refinery skins, to furnish the lead required for marketable antimonial lead. The blast-furnace equipment consisted of two five-tuyère 42-in. round furnaces, connected by a flue to the baghouse. On account of the high zinc and arsenic content in lead refinery by-products, a slag of the composition SiO_2 , 26 per cent; FeO, 40 per cent; CaO and ZnO, 20 to 24 per cent, was maintained. An average analysis of slag for 6 months showed that it contained Sb, 0.6 per cent and Pb, 2.36 per cent. The actual blast-furnace loss amounted to 2.4 per cent Sb and 1.50 per cent Pb. The furnace charge varied from 2500 to 3000 lb. with 13 per cent coke. Blast pressure was maintained at 10 to 12 oz. The two furnaces smelted 60 to 90 tons of lead and antimonial material per day, producing 30 to 35 tons of antimonial lead of the following composition: Sb, 13 per cent; Cu, 0.15 per cent; As 0.75, per cent; Pb, 86.1 per cent.

Antimonial Lead.—One example of production in the United States is at the Pittsburgh Plant of Federated Metals Co., where a circular blast furnace 42 in. diameter at the tuyères, with 10-ft. water jackets, treats approximately 100 tons per day of smelting stock made up of antimony-bearing lead battery plates and lugs (carrying 69 to 92 per cent Pb and about 4 per cent Sb), antimony ore, returned slag, limerock, 8.0 per cent coke, and 4 to 5 per cent scrap iron. Blast pressure is 24 oz. The antimony ore used has about 40 per cent Sb, 1 per cent Pb, and the antimony recovery is about 85 per cent of the total antimony smelted. The products are approximately

¹ HULST, Treating Antimony Ores, *Chem. & Met. Eng.*, Vol. 21, p. 727, 1919.

71 per cent antimonial lead metal (carrying 88.4 per cent Pb, 11.3 per cent Sb), 17 per cent discard slag, 2.3 per cent matte, and 10 per cent fume and dust.

Converters.—Sulphide ore of antimony can be smelted in a converter into which air is blown, but this is not a method in practical use. The air burns part of the sulphur of the ore, with the production of sulphurous acid and the metal itself. Antimony sulphide fumes are formed also, and these, if acted upon by a current of air, give antimony oxide:

The Hodson-Wang Process of Antimony Smelting.—An interesting combination of accepted methods of ore reduction is found in the Hodson-Wang continuous "flash" process,¹ which process utilizes the heat of the reduction reaction and also permits

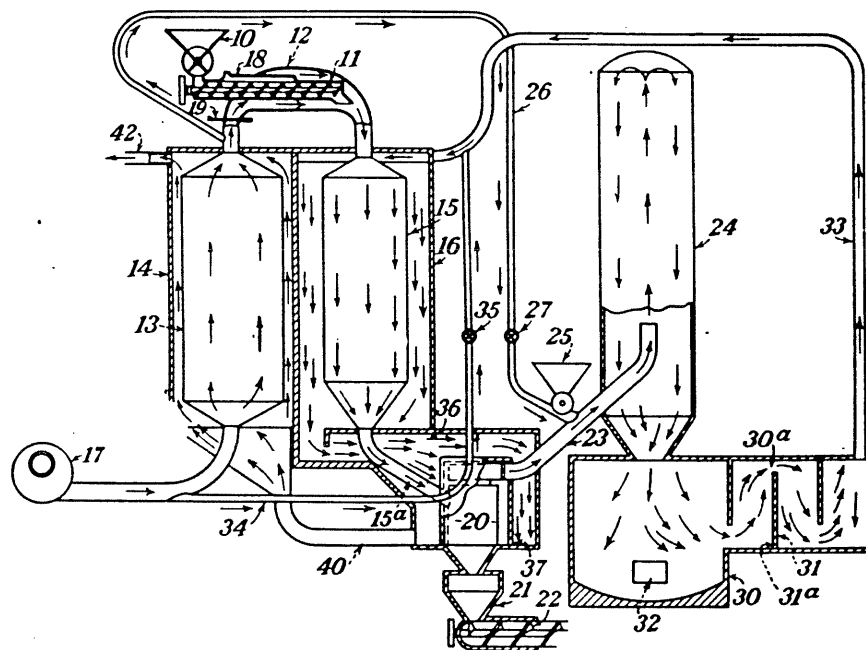


FIG. 18.—Hodson-Wang antimony process.

removal of all gangue from the ore during roasting treatment. Pulverized ore is generally used, although one adaptation of the process is designed for use of lump ore. The crude ore is roasted in an externally heated vertical or horizontal chamber by waste gases from the reduction furnace. Antimony in the ore is carried off to the main reduction chamber as trioxide gas, and all gangue matter drops to the bottom of the first chamber. The volatile trioxide formed is injected directly into a vertical shaft furnace with gaseous media (or with preheated air and carbon), and the mixture of reducing gas and oxide particles is kept in violently turbulent motion by a sudden reversal of direction. This agitation in the reducing gas promotes speed of reaction and prevents formation of an envelope of nonreducing gas around the oxide particles. The reduced metal, in fine liquid form, is collected in a lower chamber. With arsenical ores, usually sulphide, the arsenic forms volatile arsenic trioxide in the first, roasting, chamber together with the antimony trioxide. It will be reduced along with anti-

¹ (U.S. patent 2295039, Sept. 8, 1942.) Granted in the United States, Canada, Mexico, and Bolivia; applied for in Italy, Japan, Germany, Brazil, Belgium.

mony in the second chamber. However, as arsenic sublimes at a temperature of 615°C. and the reduction furnace is kept at about 800°, the antimony condenses out as a liquid, while arsenic remains a vapor and can be carried off with the gases for subsequent collection.

By-products of Antimony Smelting.—The by-products produced in the foregoing processes include liquation residues, matte, slags, and flue dust. The slags obtained from the extraction by the roasting and reduction method consist principally of silicates; those from the precipitation method, silicates and sulphides. They are thrown away if not sufficiently rich to be used in the first smelting of the ores. The other by-products are all added to the charges in smelting the ores, the liquation dross being first roasted. The flue dust is intimately mixed with soda ash, before smelting. Liquation residues are also sometimes treated separately in shaft furnaces.

The extraction by wet methods of antimony from its ores has had much attention in European centers, but it is still a matter of academic discussion, rather than practical application. Solution of stibnite is readily effected in sodium sulphide, sodium hydroxide, or calcium sulphide, and from such solutions antimony sulphide is precipitated by carbon dioxide or sulphurous acid. There is little evidence, however, that commercial recovery of antimony from its ores by wet methods has come about.

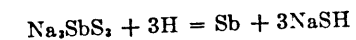
It is recognized that in the treatment of ores containing a mixture of the sulphides of antimony and lead, it would be difficult to separate the two metals. The study of Wagenmann¹ establishes the fact that in order to separate the lead sulphide from such a mixture by a solution of Na₂S, the two sulphides present in the mixture must satisfy the chemical formula 2PbS.Sb₂S₃ or Pb₂Sb₂S₃ so that the reaction Pb₂Sb₂S₃ + 2Na₂S = Na₄Sb₂S₃ + 2PbS would take place. In other words, when the Sb₂S₃ in the mixture is less than 41 per cent, enough Sb₂S₃ must be melted with the mixture in order to bring it up to 41 per cent.

Electrolytic Extraction of Antimony.—The supply of antimony for the world's needs to date has come almost entirely through the application of dry methods. Poor antimony ores either have not been used in the past, or have been subjected to a volatilizing roast, with subsequent reduction of the trioxide, usually in reverberatory furnaces. This is, however, a somewhat laborious metallurgical operation, and the application of electrolytic methods as a means of extraction from poor ores has long been desired.

During the high-price years, a small electrolytic production occurred, the solvent being a 6 per cent sodium hydroxide solution, which gives an extraction without serious contamination with other metals.

This solution, electrolyzed, deposits antimony of a very high purity, but in ordinary times the deposition of the antimony and the necessary regeneration of the electrolyte are too costly to make the process commercial. The chief difficulty is a troublesome accumulation of thiosulphate at the anode, which blocks the commercial success of the electrolytic process. *How about a diaphragm cell?*

When the solution is electrolyzed, the reaction at the cathode seems to be



while at the anode, sodium thiosulphate and Na₂S₂ are formed by oxidation. The 6 per cent NaOH solution holds about 3 per cent antimony at first, but as thiosulphate accumulates, the solvent power decreases until there has accumulated one atom of sulphur for each atom of sodium present, when the solvent power has dropped to about 0.7 per cent. When this amount of sulphur has gone into solution, the iron anode commences to be attacked and falls to pieces rapidly. A practical insoluble

¹ BORCHERS, Zinn, Wismut, Antimon. "Metallhüttenbetriebe." Vol. 4 pp. 134-136. W. Knapp, Halle, 1924.

anode has not been found. The continuance of the process beyond the point at which the sulphur in solution commences to be in a larger atomic percentage than the sodium requires the regeneration of the solution, or furnishing a new one. If a new solution is applied, it means the consumption of 1 lb. of NaOH per pound of antimony.

The best way to handle this situation seems to be the proposal by Demorest to evaporate the solution to dryness with exhaust steam; roast the residue in a reverberatory furnace to get rid of about half the sulphur, thus changing the thiosulphate to sulphate; then mix with coal and heat until it has all been reduced to Na₂S, which quickly dissolves stibnite and can be put into the circuit again. Small-scale experiment shows this to be successful, but it has not been tried on a large scale.

J. Koster and M. B. Royer¹ have developed a novel electrolytic process for the treatment of antimonial gold concentrates from ores found in the Yellow Pine Mine at Stibnite, Idaho, of the following composition: Au, 1.66 oz. per ton; Ag, 6.34 oz. per ton; Sb, 15.6 per cent; As, 5.5 per cent; Fe, 19.1 per cent; S, 25.0 per cent. This concentrate was first smelted with iron and soda ash in the proportion of 4:1:1; the crude metal obtained, to be cast into anodes, had this composition: Au, 8.4 oz. per ton; Ag, 14.6 oz. per ton; Sb, 60.7 per cent; As, 7.5 per cent; Fe, 27.4 per cent; S, 5.9 per cent.

"The electrolyte was prepared either by solution of antimony metal in sulphuric acid, evaporating to fumes of SO₃, and solution of the white pasty mass in concentrated hydrofluoric acid; or solution of antimony oxide in concentrated hydrofluoric acid, filtering undissolved matter, adding concentrated acid, and diluting to 80 g. Sb and 500 g. sulphuric acid per liter."

The crude metal from the smelting operation was cast into anodes in vertical molds 4 × 7 × ¾ in. The cathodes were of 16-gauge sheet copper and were ¼ in. longer and ½ in. wider than the anode. The most satisfactory current density was found at 6 amp. per sq. ft. Current efficiency was found to be 99 to 100 per cent.

The cathode metal was found to have the following analysis: Au, trace; Ag, 1.1 to 1.5 oz. per ton; Sb, 91 to 96 per cent; As, 3 to 7 per cent; Fe, 0.2 to 0.4 per cent; S, 0.06 to 0.09 per cent. This cathode metal, after purification by fusion with slag consisting of equal parts of NaOH, NaCl, Na₂CO₃, and NaNO₃, followed by a starring fusion with 3 parts K₂CO₃ and 2 parts Sb₂S₃, was found to have an analysis of Sb, 99.73 per cent; As, 0.19 per cent; Fe, 0.06 per cent; S, 0.02 per cent. The anode slime, containing most of the precious metals, was found to have an analysis of Au, 70 to 133 oz. per ton (80 to 94 per cent recovery); Ag, 114 to 237 oz. per ton (30 to 48 per cent recovery); Sb, 4 to 8 per cent; As, 6 to 24 per cent; Fe, 35 to 45 per cent; S, 14 to 28 per cent. The matte from the precious smelting contained, upon analysis: Au, 0.26 oz. per ton (7 per cent recovery); Ag, 5.9 oz. per ton (50 per cent recovery); Sb, 3.1 per cent (11 per cent recovery); As, 0.8 per cent; Fe, 52.6 per cent; S, 32.1 per cent. The recovery of antimony was found to be 80 to 90 per cent, from concentrate to marketable metal.

Electrolytic Antimony.²—At the Bunker Hill and Sullivan Mining & Concentrating Co., Idaho, tetrahydrite, 3Cu₂S.Sb₂S₃, concentrates mixed with Na₂CO₃, Na₂SO₄, and coal are fed to a three-electrode electric furnace. Current, at 50 to 110 volts, flowing from electrode to furnace wall, the charge serving as the resistance, yields a melt temperature of about 2300°F. Matte is tapped from the furnace, cooled, and crushed to pass 80 mesh. The ground matte is leached with sodium sulphide solution at 140°F. to form the electrolyte. Undissolved pulp is crushed and tabled to yield a concentrate of Sb-Bi-Ag alloy and a tailing containing 25 to 30 per cent Cu and 1 per cent Sb, the latter being added to the copper-smelter charge. From the electrolyte

¹ Electrolytic Recovery of Antimony from Antimonial Gold Ores, U. S. Bur. Mines Rept. Investigation 3491, February, 1940.

² Mining World, Vol. 4, No. 6, pp. 3-9, 1942.

Sb &
Au
Electrical
Recovery

containing the thioantimonate, Na₂SbS₄, antimony is deposited on sheet steel cathodes, the anodes being sheet lead. The anodes are in a compartment formed of heavy sail cloth as a diaphragm. There is no material corrosion of either electrode at operating current density of 20 amp. per sq. ft. Cathodes are stripped of their antimony each 6 days. Spent electrolyte containing about 2 to 5 g. per l. is recycled back to the leaching tanks after a treatment with sufficient barium sulphide to precipitate the sulphate ions present. The precipitated barium sulphate is reduced to sulphide for re-use as a precipitant. The antimony, being brittle, is easily removed from the cathodes. This plant, erected at a cost of about \$500,000, started operations in March, 1940.

Refining of Antimony Metal.—Unrefined antimony usually contains sulphur, iron, arsenic and copper, and lead. These impurities, with the exception of lead, can be eliminated partly by oxidizing and slagging agents, partly by sulphurizing agents, and partly by chlorinating agents. Soda, potash, or antimony glass (antimony oxy-sulphide) removes sulphur by fusion and converts arsenic into arsenate of soda or potash. The conversion of copper and iron into their sulphides by sulphide of antimony can be facilitated by the addition of soda or potash, or of Glauber's salt and charcoal. These sulphides form a slag with the sulphide of sodium produced from the reduction of the Glauber's salt, with the soda or potash present. These sulphides are easily removed by antimony glass.

The use of common salt, carnallite, or magnesium chloride to volatilize some of the foreign metals present as chlorides, and to slag others, may occasion great loss of metal due to volatilization. It is somewhat difficult to remove the lead, and when antimony ores are found to contain a considerable percentage of lead, as is frequently the case, they may with advantage be smelted with lead ores to produce hard, or antimonial, lead (12 to 15 per cent Sb).

One of the most objectionable impurities found in antimony is arsenic, because great loss of the metal and expense are entailed when one tries to bring the arsenic down to the market tolerance. Obviously, the best way to obviate this difficulty is to free it as much as possible from the ore before it is smelted. This can be done by differential flotation of the arsenic mineral, as will be described later, or as suggested by Koster and Royer,¹ by roasting the ground ore or concentrate at 475 to 500°C. with steam at atmospheric pressure, when approximately 88 per cent of the original arsenic will volatilize off with only a loss of about 10 to 15 per cent antimony.

If the antimony oxide, obtained in the volatilization process, contains arsenious oxide, say as high as 2 to 3 per cent, the following method can be adopted for its partial elimination.

1. Heat the oxide in a muffle furnace to above 200°C. whereby the As₂O₃ is volatilized while the Sb₂O₃ may remain as Sb₂O₃ or partially change to Sb₂O₄. Constant rabbling is necessary. In an experiment by C. C. Chao in the laboratory of the National Bureau of Mining and Metallurgical Research, China, the arsenious oxide was brought down from 2.38 to 1.55 per cent at a temperature of about 300°C.

2. The arsenious oxide can be brought down from 2.38 to 0.54 per cent by digesting the antimony oxide with hot water and 0.5N HCl for 4 to 5 hr.

To reduce the amount of arsenic contained in the regulus, the following method can be adopted. After covering the molten metal with soda ash, air is blown into it. In three successive operations, occupying about 2 hr., the arsenic content can be brought down from 1 to 0.1 per cent. The soda ash used is about 2½ per cent by weight of the bath in each operation. The soda ash in the slag produced can be regenerated by a simple process.

¹ U. S. Bur. Mines Rept. Investigation 3491.

A similar method of refining antimony by blowing air through the molten metal has been worked out by G. A. Merson, L. Ya Krol, and O. E. Krein.¹ According to them, the following optimum conditions are recommended for carrying out the refining treatment, which reduces the arsenic content in the metal from 0.70 to 0.05 per cent.

1. Temperature—950°C.
2. Air supply for blowing—500 ml. per min. per kg. of metal.
3. Amount of soda slag—20 per cent; the slag is renewed once during refining.
4. Duration of refining—1 hr. under each slag, *i.e.*, a total time of 2 hr.

Under the above conditions a yield of 89.5 per cent refined antimony was obtained. Of the remaining 10.5 per cent, 8.75 per cent passed into the slag, while 1.75 per cent volatilized off as Sb_2O_3 .

Another method to refine antimony containing an appreciable amount of arsenic is to melt the metal, which is crushed to 10 to 15 mesh with, say, 5 per cent niter and about the same amount of soda ash.

Starring.—It has long been the practice of the trade to judge the purity of refined antimony by the development of a fernlike structure, or "stars," on the surface of the ingot. The appearance of this structure does not actually indicate the relative purity of the metal, but is only the result of cooling it slowly under cover of a layer of a properly prepared starring mixture—couverture—a slag that has a fusion point lower than that of antimony, which is 630°C. When the regulus contains impurities like sulphur, arsenic, lead, or iron, to any appreciable extent, its surface shows the presence of these foreign elements by specks, by a leaden appearance, or by a poorly defined appearance of the fernlike structure. It is true, on the other hand, that regulus containing impurities above what are considered to be the limits imposed by the market often shows stars as bright and well defined as those of well-refined regulus. Since buyers demand this artificial adornment on the regulus, the starring operation has become a regular part of the refining process, adding an unnecessary cost of \$5 to \$30 per ton.

Different mixtures for this couverture are shown in Table 2 by the authors, as used, according to local conditions, by various antimony smelters in China.

Another starring mixture for pure Chinese ores, patented by C. Y. Wang in 1918 with the object of avoiding the use of mixtures containing any antimony compound, utilizes iron sulphide, which is generally discarded from the precipitation process of antimony smelting as useless. This by-product takes the place of antimony compound and is used with any suitable alkali compound, preferably potassium carbonate. The proportions of the mixture are as follows: iron sulphide, 9 to 14 parts; potassium carbonate, 8 parts.

In England the process of refining and restarring the star bowls, also a pot-furnace operation, is as follows: The lumps of metal, when cold, are removed from the mold and are thoroughly cleaned from the adhering skin of slag by chipping with sharp hammers, this part of the work being sometimes done by women. Unless this cleaning process is carefully done, it is well-nigh impossible to obtain good stars on the finished metal. The chippings are returned to the second smelting. Having been cleaned, the star bowls are broken small. The charge made is about 84 lb., together with enough flux to surround the ingots completely; the quantity is generally 8 lb. for ingots of the ordinary shape. The melting takes place in the crucibles standing close to the fireplaces, where the fusion is most rapid. The metal is charged first and is closely watched; as soon as it begins to melt, the flux is added; and as soon as the fusion appears to be complete, the furnaceman stirs the mixture once round only, with an iron rod, and the charge is then poured out. The flux is used over and over again,

¹ *Jour. Applied Chem. (U.S.S.R.)*, Vol. 13, pp. 323-328, 1940; abstracted in the *Metal Ind. (London)*, June 13, 1941, pp. 505-506.

being regenerated by the addition of carbonate of potash. The ingots must be completely surrounded by the flux; there must be a thin layer of it between the mold and the metal, and also the whole surface of the ingot must be covered by the flux to a depth of $\frac{1}{4}$ in. Any traces of the flux still adhering to the ingot are removed by washing in warm water, with the assistance of a little sharp sand.

TABLE 2.—COUVERTURE MIXTURES

Couverture	Crude (high-grade), Sb_2S_3	Antimony tetroxide (well-roasted crude), Sb_2O_4	Antimony trioxide, Sb_2O_3	Potash, K_2CO_3	Soda ash, Na_2CO_3	Charcoal, C	Smelters using the mixtures
I	15	24	...	10	1	1.25	Pao Tai
II	15	24	...	11	3	1.25	Pao Tai
III	2.2	13.2	...	7.5	...	5.7	To-cheng
IV	4.5	...	20	...	5	0.5	Loong Kee
V	7	...	18	...	4	0.5	Tai Wo
VI	3-4	...	32	...	2-4	1	
VII	5	30	5-6	1	Pao Tai
VIII	85	...	15	...	Wah Chang
IX	4-5	1-2.5	Wah Chang
X	8	1	
XI	40	1	4	...	
XII	7	...	1	...	Loong Kee
XIII	6	...	16*	...	1	0.5	Pao Tai
XIV	7	14	0.5	0.5	Pao Tai

* Pure flue dust.

For a charge of 60 to 70 lb. of bowl metal, with 1 to 2 lb. of potash and 10 lb. of slag, obtained from a previous charge of French metal, the time required is $\frac{3}{4}$ hr.

Refining in Reverberatory Furnaces.—The refining operation is in most cases carried on in a small furnace, of reverberatory type, and proceeds about as follows: 1200 to 1500 lb. of impure antimony is melted as one charge, to which is added 3 to 7 per cent of soda, mixed with a little coke dust or fine charcoal. The slag from this fusion gradually becomes thicker and thicker, and after about 3 hr. is skimmed off through the working door. Up to this point, the iron and sulphur remain as impurities in the metal. They are next removed by adding ingredients capable of forming antimony glass, such as oxysulphide of antimony. For each 100 lb. of antimony in the charge, 3 lb. of liquated sulphide of antimony and $1\frac{1}{2}$ lb. of antimony tetroxide are thrown in, and as soon as these are fused, $4\frac{1}{2}$ lb. of potash is added. Care is taken that the bath of metal is completely covered with the fluxes.

The metal can be ladled out, after another 15 min., being handled cautiously, in order to secure the starred appearance of the ingots. Three charges of about 1500 lb. each can be refined in one of the small furnaces used, in 24 hr., with a coal consumption of 1300 lb.

The slag obtained in the final step of the refining operation is called "star slag" and consists principally of antimony glass, carrying 20 to 60 per cent antimony. It is used repeatedly for refining, until it becomes too impure for the purpose, when it is

charged along with the ore for the first smelting. The other slags obtained in the course of refining are also added to the ore-smelting charges.

The proper procedure for charging any of the above mixtures is as follows: The compound, after being thoroughly mixed, is immediately charged into the reduction furnace as soon as the skimming is finished. The doors are closed, and vigorous firing is maintained; as soon as it is observed that the mixture is completely melted, ladling commences. Each ladle dips into the molten metal and, in coming out, picks up a certain quantity of the molten couverture, which, when poured out together with the metal into a hold mold, completely covers the metal on all sides. Ladling must be done rapidly for each moldful—four or five ladles to one slab of regulus according to the size of the ladle used. The thickness of the solidified couverture varies from 1 to 2 mm. on all sides except the top, which varies from 5 to 7 mm. The amount of couverture required for each charge varies from one-sixth to one-fourth the weight of the regulus produced. It is remarkable that generally the weight of the solidified couverture hammered off from the slab after cooling is less than the original weight of the mixture put in by about one-third, owing in part to volatilization and in part to wall-fluxing during melting. The couverture can be used over again the second or third time, sometimes with an addition of a little soda, until it is so contaminated with impurities that it cannot produce any good stars. Then the worn-out couverture is mixed with the ordinary charge of trioxide or tetroxide and calculated as an equivalent amount of soda required for that charge. In connection with this, the practice at the Loong Kee and the Pao Tai smelters may be mentioned: The Loong Kee smelter uses, for every 14 tons of regulus produced, 1.14 tons of couverture which, according to couverture XII of Table 2, contains 1 ton of trioxide and 0.14 tons of soda. The Pao Tai smelter uses 1 ton of couverture XIV for 14.5 tons of regulus.

TABLE 3

Name of brands	Sb	Cu	Fe	Pb	As	Sn	Zn	S	Others
W. C. C. (Chinese)	99.848	Trace	0.009	Trace	0.095	0.030	Trace	0.018	Cd, trace
Hallett's	99.856	0.046	0.007	0.718	0.210	0.012	0.023	0.128	
Cookson's	99.608	0.046	0.004	0.102	0.092	Trace	0.034	0.086	Co, Ni 0.028
Japanese	99.195	0.043	0.007	0.424	0.095	0.012	0.023	0.201	
Chinese	99.760	0.012	0.004	0.029	0.090	0.027	0.078	Co, Ni, trace
La Lucette	99.35	0.010	0.060	0.130	0.200	0.200	
U. S. "Lone Star"	99.70	0.050	(No other single impurity in excess of 0.10 per cent)			
U. S. "R.M.M."	99.30	0.10	excess of 0.10 per cent)			
Czechoslovakia	99.70	Trace	0.110	0.04	0.070	0.050	
	99.70	Trace	0.056	Trace	0.031	0.119	Ni, Sn, trace
Yugoslavia	99.34	0.11	0.04	0.30	0.080	

NOTE: English antimony generally commands a premium over foreign brands, especially the "C" Brand of Cookson's, which is recognized as the world's standard antimony.

A procedure, as adopted by W. Brazenall¹ for starring the regulus produced, is as follows: "The flux furnace was 4 × 3 ft. It was heated by wood fuel, and kept at a low temperature. It was tapped into a large pot and ladled out by small ladles into the metal ladles just before pouring. The metal ladles were placed under the taphole of the metal furnace, one on the floor and the other on bars above it, close to the spout of the furnace. Then the bar was drawn, allowing the metal to flow into the ladles, into which enough flux had been poured to cover two bars. The molds,

¹ Chem. Eng. Mining Rev., June 6, 1932.

10 × 10 × 3 in., were placed in rows adjoining each other, and a gate of iron was placed above them with a hole at each end reaching to the center of the molds, so that both molds were poured simultaneously. The flux floating on top of the molten metal flowed into the mold with the metal, thus completely covering it. This is essential for starring the metal, as it excludes the air from it. This method of pouring the metal was devised by the writer Brazenall at the works of the Western Metal Co., Harbour City, Calif., after a great deal of experimentation, in order to avoid ladling from the furnace with iron ladles, as they soon wear out and burn away, the iron then going into the metal."

Typical analyses of refined antimony supplied by English, Chinese, American, French, Czechoslovakian and Yugoslav producers are shown in Table 3.

Ore Dressing.—Beneficiation of low-grade sulphide ores of antimony by means of ore dressing has been tried both experimentally and in practice and has given indication that in the future it will form a beneficial adjunct to metallurgical treatment.

It is undeniable that it is better to free the arsenic, if present in the antimony ore in an appreciable quantity, at the very beginning by differential flotation before smelting than, to resort to the laborious and expensive methods of treating the final metal for its elimination.

There occur, in many parts of the world, scattered deposits of low-grade ores of antimony for which the building of a metallurgical plant is unwarranted. For their exploitation, beneficiation of the ores is highly desirable in order that the concentrates be profitably shipped to other centers for metallurgical treatment. Sometimes, associated with the antimony ores are gold and silver, which, in the same dressing operation, are at the same time concentrated. But the general problem of concentrating low-grade oxide ores of antimony is still awaiting solution.

A few instances of past experiments and current practices are now given, to show the trend of the development of the dressing of antimonial ores.

The Flotation Plant at Djinli Kaya Mine in Turkey.—The flow sheet is as follows: From ore bin to ball mill about one of water to two of ore by weight was used. The mill discharge passed to the Dorr classifier, and sufficient water was added here to make a pulp of 2½ or 3 of water to 1 of ore. The pulp passed to the larger steady head tank where more water was added when required to bring the dilution up to 4 of water to 1 of ore, and thence to the fourth cell of a 12-cell flotation machine. The reagents used were creosote, naphtha, cresylic acid, xanthate, cyanide, soda ash, lime. The use of reagents depended on the type of ore to be treated and the acidity or alkalinity of the water available. It was essential that the pulp be slightly alkaline. The ore consisted of 10 to 20 per cent Sb and 0.5 to 10 per cent pyrite in a relatively soft siliceous gangue. The mine water used had to be neutralized by the addition of soda ash or lime.

A concentrate carrying 60 to 65 per cent Sb and tailings of 1 to 2 per cent Sb was aimed at. Cyanide was used to depress the pyrite. The function of the creosote, oils naphtha, and cresylic acid was mainly to coat the small bubbles of the froth to which the shining particles of sulphide adhered. Xanthate was most useful in cleaning up the tailings. Very little, if any, of this reagent was used before the pulp had reached the seventh or eighth cell of the machine, the froth from these cells being returned to the machine and refloats. The order of the feed of the reagents was as follows: Mixture of creosote and cresylic acid in ratio of 1:2 at 4 lb. per ton to No. 4 cell; cyanide at 0.5 lb. per ton to No. 1 cell; lime or soda at 0.6 lb. per ton to overflow from classifier.

Differential Flotation Work at the Wiluna Gold Mine, Wiluna, Australia.²—A bulk concentrate containing arsenic and iron sulphide together with antimony is

¹ LAWRENCE, *Mining & Met. Soc. Bull.* Vol. 7, July, 1933–March, 1934.

² Private communication.

floated in a Fagergren machine. The antimony content of the feed to this machine varies from 0.2 to 2 per cent. The bulk concentrate contains 4 to 20 per cent, depending on the grade of the crude oil.

Xanthates and lead sulphate with pine oil and cresylic acid are the reagents used in this circuit. Alkalinity is controlled by the addition of soda ash. The bulk concentrate is then passed to a series of cleaning machines where the pyrite (and arsenopyrite) is depressed by the addition of caustic soda and cyanide and other reagents. The success of the operation depends on the accurate control of depressants in the first stage and, subsequently, the control of depressants in the cleaning circuit and the points where they are introduced. To produce a 60 per cent Sb concentrate, 6 to 10 cleaning operations are necessary.

Differential flotation of an arseniferous-sulphide ore of antimony, containing gold, has been practiced at the Cucuma mine, Czechoslovakia.¹ For the flotation of 1 ton of 6 per cent Sb ore to concentrates containing 60 per cent Sb, the following reagents were required: H₂SO₄, 8800 g.; xantol, 80 g.; ethyl xantogen, 115 g. To separate the associated arsenic, the reagents required were: Na₂S, 345 g.; Na₂CO₃, 580 g.; sapinol, 42 g.; butyl xantogen, 115 g.

The Yellow Pine Mine, Stibnite, Idaho,² uses flotation to concentrate the gold-silver-antimony ore. The heads averaged 1.85 per cent Sb, \$4.75 in gold, and about ¼ oz. of silver per ton. The following reagents were used in the flotation of stibnite:

	Pounds per Ton
Copper sulphate.....	1.21
Soda ash.....	0.03
Caustic soda.....	1.37
Chlorine.....	0.82
Cresylic acid.....	0.30

Flotation resulted in a stibnite concentrate containing 0.77 oz. per ton of gold, \$10.51 in silver, and 48.60% antimony.

Dry Concentration.—It is known that wet gravity concentrations of antimony ore with jigs and tables give rise to much slime loss. Experiment with dry concentration on dry concentrating tables, such as those manufactured by Sutton, Steele & Steele, Inc., Dallas, Tex., has shown that it is possible to concentrate a sulphide ore of antimony containing 8.56 per cent Sb to concentrates containing 65 to 70 per cent Sb and middlings containing 22 to 30 per cent Sb, which together represent 88 per cent recovery. The antimony content of the tailings amounts to 0.60 to 1.30 per cent Sb. The optimum size for this particular ore was found to be minus 28 to plus 35 mesh.

It is generally felt that antimony oxide ore does not respond to flotation. The Adelaide School of Mines, however, has recently found that it is possible to float cervantite at pH 7 after sulphidizing with sodium sulphide.

Résumé of Antimony Metallurgy.—The sulphide ore, stibnite, is the only ore of practical importance; the oxide ores, valentinite, senarmonite, or cervantite, being of minor significance. Beneficiation of low-grade ores by gravity concentration, air concentration, and flotation is under way or planned in all the producing regions where freight to distant smelting points must be considered or where the ore contains valuable constituents other than antimony. In the case of an ore containing an appreciable amount of arsenopyrite, it is sometimes advisable to use differential flotation to get rid of the arsenopyrite, which would otherwise contaminate the product resulting from the pyrometallurgical treatment of such ore. Of all the concentration methods, flotation appears to be by far the most satisfactory method and will undoubtedly find a place in antimony processing.

¹ Private communication.

² U. S. Bur. Mines Information Circ. 7194, January, 1942.

As a rule, concentration methods for antimony minerals have in the past shown unsatisfactory percentages of recovery due to dust losses. The relatively high frangibility of antimony ores results in heavy dusting, at crushers and screens, and the metal content of the dust is unusually high. For example, in dust from ore carrying 5 to 6 per cent metal, the metal content collected in dustproof housings and baghouse has been found concentrated to 15 to 20 per cent. The amount of dust collectible from antimony ore properly trapped may be as high as 10 per cent of the ore treated. In plants now under discussion, this type of dust will be concentrated by delivering it to the flotation cell along with the finer ore screenings. Dustproof housings installed with air concentrating tables are expected¹ to extend the use of dry concentration (air flotation) in many low-grade antimony districts.

As to hydrometallurgical or electrolytic methods of extracting antimony, they are uneconomical and only under exceptionally high prices and special circumstances may their adoption be recommended.

It is to be emphasized that, whatever smelting method is followed, an antimony plant must have a particularly good flue and condensing system. We know that with ordinary settling devices, such as flues with reduction or expansion of cross sections, Freudenberg plates or Roesing wires, only dusts larger than 10 microns (10⁻³ cm.) can be deposited; hence antimony fumes, whose particles range from 0.3 to 1.0 micron, and settle very slowly even in still air, cannot be effectively deposited. The usual cyclone dust catcher acts very ineffectively with antimony fumes; even the best cyclone, the so-called multiclone,² cannot settle particles smaller than 5 microns. Filtration of antimony fumes by means of bag filters, woolen or cotton, has been more or less adopted in many antimony works.

The Cottrell process of electrical precipitation has been adopted in a few antimony works and has proved its worth as a secondary cleaner for the oxide fumes.

The scrubbing or washing of antimony fumes, involving, as it does, the intimate mingling of the fumes by means of sprays or jets of water, is not thoroughly effective in precipitating the oxide. However, the Peabody process,³ as recently developed in England, is a distinct improvement on the old-time scrubber and is a device that may be applicable to the condensation of antimony fumes.

For different grades of ore, the following methods are generally adopted:

1. For sulphide ore containing about 20 per cent Sb, the volatilization method.
2. For sulphide ore containing about 35 per cent Sb, the blast-furnace method.
3. For sulphide ore containing about 50 per cent Sb, the liquation method and the English precipitation method.
4. For oxide ore containing about 30 per cent Sb, the blast-furnace method.
5. For oxide ore containing about 50 per cent Sb, the direct reduction method.
6. For mixture of sulphide and oxide ore, the blast-furnace method.

It is to be noted that dead roasting of sulphide ore to the stable tetroxide, as a process for the treatment of rich ore, has become obsolete.

Production Economics.—The average yearly world production of antimony, including crude and oxide in Sb content, during the period from 1908 to 1938 was about 27,700 metric tons (China 62 per cent, Mexico and Bolivia, each about 11 per cent, totaling about 84 per cent of the world production, leaving about 16 per cent supplied by the United States, Algeria, France, Czechoslovakia, Italy, Yugoslavia, Peru and Argentina, with insignificant outputs from other countries).

¹ Allen H. Smith, patent pending.

² For an analysis of mechanical methods of dust collection see LISSMAN, *Chem. & Met. Eng.*, October, 1930, pp. 630-634.

³ R. R. HARMON, Removal of Suspended Matter from Industrial Gases, *The Institute of Fuel*, London, April, 1938.

Increased demand, war born, for strategic metals has been coincident with global shifting in sources of raw material. In no commodity has the supply picture shifted more extensively than for antimony. In comparison to the normal movement of 65 to 70 per cent of world supply from China and 30 to 35 per cent from other sources in the 8 years prior to the Sino-Japanese War, the years of 1942 and 1943 draw approximately 49 per cent of world production of new metal from Mexico, 35 per cent from Bolivia and Peru, 14 per cent from the United States, and 2 per cent from various other regions. This is a forced draft on these last-named world areas, and it is believed probable that postwar economics will turn the searchlight back to the preponderant Chinese supply. Though actual Chinese export to the United Nations has dwindled to almost nothing, production in the Asiatic fields has continued in varying degrees as a matter of national economy and human livelihood, and Chinese stock piles of antimony—ore and metal, exact quantities unknown—are accumulating as a cushion for such postwar raw-material exhaustion as may develop.

Return of commodity normalcy, postwar, is expected to register, in the antimony industry: (1) 25 per cent shrinkage, by and large, of current world demand; (2) inability of Western Hemisphere areas, recently prolific, to maintain preponderance of supply; (3) reversion to Asiatic supply area.

Under normal conditions the relatively high cost of production in the United States from labor and deposit angles prevents successful competition with Chinese metal. The antimony-producing countries of the world may be divided into three groups:

1. Principal potential production, in order of importance: China, Mexico, Bolivia.
2. Irregular in normal times but with potential reserves available at higher price levels: The United States, Yugoslavia, Peru, Czechoslovakia, Algeria, Italy, Australia, French and Spanish Morocco, Canada, Turkey (Asia Minor).
3. Production small, known reserves probably less important: Hungary, Russia, Argentina, Portugal, Burma, Indo-China, British India, Japan, Southern Rhodesia, South Africa, Borneo, Greece.

CHAPTER VI

BISMUTH

BY WALTER C. SMITH¹

History.—The metal bismuth has been known since the Middle Ages. Agricola refers to it as a form of lead and describes a method of separation from its associated minerals by liquation. The impure bismuth of the early writers was often confused with antimony, tin, and zinc. During the eighteenth century, bismuth was identified as a metallic element.

Occurrence and Properties.—Bismuth is rather widely distributed, but is not an abundant metal. It occurs as native metal, oxide, carbonate, sulphide, and as a constituent of many complex minerals. The supply of bismuth is derived from two principal sources: (1) bismuth ores mined and treated for their bismuth content; (2) ores mined and treated primarily for other metals in which bismuth is a minor constituent and from which it is recovered as a by-product.

Bismuth is a coarsely crystalline brittle metal, tin white in color, but with a distinct reddish tinge and a high luster. It has the atomic number 83 and an atomic weight of 209. Bismuth crystals are trigonal or rhombohedral. Bismuth crystallizes in a rhombohedral face-centered or deformed simple cubic lattice; the lattice constant $a = 4.726$ angstrom units. The unit rhomb contains 8 atoms.²

The density of bismuth is 9.80 g. per cc. at 20°C. and 10.067 at the melting point. The density of molten bismuth decreases regularly as the temperature rises, from 10.062 g. per cc. at 275°C. to 9.611 at 650°C. Expansion of the metal during solidification amounts to 3.32 per cent of its solid volume at the melting point. The compressibility is 2.8×10^{-6} , between 100 and 500 megabars, when the compressibility is defined as the average fractional change of volume caused by 1 megabar pressure. The hardness of commercial bismuth is 7.3 on the Brinell scale, using a 6.35-mm. ball and a 40.3-kg. load at 20°C., and 2+ on the Mohs scale.

The melting point of pure bismuth is 271°C. The mean specific heat for the metal up to the melting point is 0.0319 cal. per g., the latent heat of fusion is 14.1 cal. per g. The vapor pressure is 10^{-3} mm. of mercury at 540°C., 1 mm. at 840°C., and 100 mm. at 1200°C. The boiling point at atmospheric pressure is between 1440 and 1500°C. The heat of vaporization is 42,700 cal. per gram molecule. The thermal conductivity varies from 0.018 cal./(sec.)(cc. per °C.) at 100°C. to 0.037 at 400°C. and higher. The thermal conductivity of solid bismuth is less than that of any other metallic element except mercury. The mean coefficient of expansion, from 0 to 100°C., is 0.00000731. The viscosity of bismuth is of the same order of magnitude as for cadmium, tin, and lead. The coefficient of viscosity at 23.7°C. is 13.71×10^8 poises (dynes per cm.²). The surface tension of bismuth is lower than that of tin, cadmium, lead, or antimony. It varies from 376 dynes per cm. at 300°C. to 343.9 dynes at 779°C.

In the electrochemical series, bismuth lies just below hydrogen, together with arsenic, antimony, and copper. From this position, bismuth is positive to such metals as lead and tin. It is less subject to oxidation than lead or tin and more resistant to corrosion under oxidizing conditions. The hydrogen overvoltage at a bismuth surface

¹ Metallurgist, Cerro de Pasco Copper Corp., New York.

² Nat. Bur. Standards Circ. 382, April, 1930.

Amphoteric
 in 2N H₂SO₄ at 25°C. is 0.388 volt, somewhat greater than the corresponding value for antimony. Bismuth electrodes show a tendency to passivity in both alkaline and acid electrolytes, and the metal is amphoteric in that it dissolves electrochemically at both anode and cathode.

The specific resistance of solid bismuth is 106.5 microhm-cm. at 0°C., as compared with 1.683 for copper. The mean temperature coefficient of resistance from 0 to 100°C. is 0.00446. Electrical resistance of the solid metal increases with pressure and decreases with tension. At the melting point the specific resistance of solid bismuth is 267 microhm-cm. and of liquid bismuth, 127. Bismuth and antimony are the only two metals whose resistance is greater in the solid than in the liquid state.

Bismuth possesses an unusual thermal e.m.f., about 80 μv per °C. against silver. By coupling pure bismuth with a bismuth alloy containing 5 to 6 per cent tin, an e.m.f. of about 120 μv per °C. can be obtained. A Thomson effect of 676 μv per °C. for an alloy of bismuth with 1 per cent tin, against copper, has been observed. The low melting point and the difficulty of preparing and maintaining wires of suitable size, owing to brittleness and lack of ductility, interfere with the thermoelectric use for bismuth.

Bismuth is the most diamagnetic of all metals, but the susceptibility decreases with rising temperature. An alloy of Cu-Mn-Bi is distinctly magnetic, although all the components are diamagnetic.

The thermal conductivity decreases in a magnetic field. The electrical resistance of bismuth increases when the metal is subjected to the action of a magnetic field.

The absorptive powers of bismuth for X rays have been measured and are similar to those of lead.

Chemical Properties.—Bismuth is not affected by air at ordinary temperature; heated in contact with air, it becomes coated with a grayish-black oxide at temperatures just below the melting point; at higher temperatures a yellow or green oxide (Bi₂O₃) is formed. Bismuth burns with a bluish flame at a bright-red heat, forming Bi₂O₃. Water does not affect bismuth at ordinary temperatures; at white heat, water vapor is slowly decomposed by it.

Bi
 Fe
 Precip
 Bismuth combines directly with chlorine, bromine, and iodine. It is not attacked by dilute sulphuric, dilute hydrochloric, or cold concentrated sulphuric acids; hot concentrated hydrochloric acid attacks bismuth slowly. It dissolves in hot concentrated sulphuric acid and is readily soluble in nitric acid or aqua regia, either hot or cold. Molten bismuth combines directly with sulphur to form bismuth sulphide, Bi₂S₃. Bismuth is precipitated from solution as metal by zinc, manganese, iron, nickel, cadmium, copper, tin, and lead. It is precipitated from solution as the sulphide by hydrogen sulphide and all the soluble sulphides. Basic salts of bismuth are precipitated from solutions of the sulphate, nitrate, and chloride of bismuth upon heavy dilution with water.

Extraction of Bismuth.—Both fire and wet methods, or a combination of both, are used for the extraction of bismuth from ores and metallurgical products. The greater portion of the production is obtained by fire methods. Bismuth produced by either method is generally too impure for use and must be refined.

Extraction by Liquefaction.—One of the earliest methods to be employed for the recovery of bismuth was liquefaction. This process was formerly used in Saxony. The liquefaction was carried out in inclined cast-iron pipes, heated with a wood or coal fire. The ore containing metallic bismuth was introduced into the pipes and the readily fusible bismuth melted and flowed out of the lower ends of the pipes, leaving the gangue of the ore as a residue in the pipes. This residue still contained considerable bismuth, and was drawn from the pipes, smelted to a bismuthic speiss, and then re-treated in the liquefaction furnace. One form of furnace carried 11 cast-iron pipes, each 4 ft. long,

10 to 12 in. high, and 6 to 8 in. wide; each pipe received a charge of about 33 lb. of ore; 15 to 20 min. were required for the liquefaction, and the furnace consumed approximately 690 cu. ft. of firewood per 24 hr.

Extraction by Fusion.—The fusion of raw or roasted bismuth ores, with carbon for reduction and the proper fluxes to yield a fusible slag, has superseded the liquefaction process. The fusion is carried out in either crucibles or small reverberatory furnaces. Metallic iron is added to the charge to decompose any bismuth sulphide in the melt. Lime, soda ash, salt cake, fluorspar, and feldspar are some of the fluxes used to give a fusible slag. The products of the fusion are metallic bismuth, matte, or speiss and slag. The melt is usually cast into molds and the three products separated after solidification. The matte or speiss retains some bismuth and is crushed, roasted, and resmelted. Crucibles made of fire clay and furnace hearths made of firebrick give the best results. The furnace hearth should be removable to permit rapid repairs.

Wet Extraction of Bismuth.—When bismuth is present in ores and metallurgical products as oxide or carbonate, hydrochloric acid is employed to dissolve the bismuth. Metallic bismuth and alloys are treated with nitric acid, aqua regia, or hot concentrated sulphuric acid. A method employed for the extraction of bismuth is as follows: Finely crushed bismuth litharge, cupel bottoms, and other oxidized material containing 5 to 20 per cent bismuth, are treated in stoneware or other suitable vessels with hydrochloric acid. The proportions are 140 to 155 lb. of hydrochloric acid and 22 lb. of water for each 100 lb. of material treated. The mixture is heated gently and stirred for 5 to 6 hr.; water is carefully added until the white bismuth oxychloride just begins to form; it is allowed to settle for 6 to 8 hr., and the clear solution is then siphoned into wooden tanks. Water is added to this solution in order to complete the precipitation of the bismuth oxychloride, and the mixture is allowed to settle. The clear liquor is siphoned off and is treated with scrap iron to precipitate any copper carried by the solution. The bismuth oxychloride is washed with hot water to remove as much lead chloride as possible, then dissolved in hydrochloric acid and reprecipitated by dilution with water. It is then filtered, dried, and smelted with lime and charcoal to metallic bismuth. The bismuth produced by this method usually contains small amounts of lead, silver, and other impurities. The leach residue, containing lead, silver, and other metals, is washed, filtered, dried, and mixed with lime or soda ash and carbon, reduced to metal, and reworked in the cupel furnace for the recovery of the silver and other values.

Electrolytic Refining.—Bismuth can be refined electrolytically. Both the chloride and the fluosilicate electrolytes have been used. The more economical fire-refining methods have largely replaced electrolytic refining.

Separation of Bismuth from Lead Bullion.—Substantially all the bismuth production of the Western Hemisphere is derived from flue dusts from copper-smelting operations or from lead ores. The bismuth-bearing dusts are generally treated at lead-smelting plants, in which case the bismuth is collected in the lead bullion.

Bismuth can be separated from lead bullion by the following methods:

1. Electrolytic refining of the lead bullion (Betts process)
2. Betterton-Kroll process.
3. Crystallization (Pattinson or Hall processes).
4. Electrolytic production of white lead (Sperry process).

In the electrolytic refining process, the lead bullion is cast as anodes and refined to very pure lead cathodes and an anode residue or slime from which the bismuth is recovered.

The slime is melted and arsenic, antimony, and more or less of the lead are removed by selective oxidation, leaving a metal containing gold, silver, copper, bismuth, tellurium, and some lead. This metal is treated by further oxidation to yield doré

Remove
Te by
Molten
Caustic
Soda

and a bismuth-copper-lead-tellurium slag. The slag is reduced with carbon to a crude bismuth metal. If present in excess, copper and tellurium can be collected in a matte, by the addition of sulphur to the melt. Salt cake and carbon, galena, or pyrite are sometimes used in place of sulphur. If the crude bismuth contains large amounts of tellurium, it is removed by successive treatments with molten caustic soda. The crude bismuth is then drossed by cooling and skimming for the further elimination of copper and tellurium. Silver, gold, and residual copper and tellurium are eliminated by zinking and skimming. The desilverized bismuth is refined with chlorine gas. When the lead has been eliminated, the residual chlorine is removed from the metal with air and the bismuth is given several treatments with molten caustic soda before casting. The refined metal should assay 99.995 per cent bismuth. All drosses and skims from the refining operations are re-treated for recovery of valuable metals.

In the Betterton-Kroll process the lead bullion is softened and desilverized by standard Parkes process methods. The desilverized lead is treated with metallic calcium or calcium and magnesium, cooled, and the calcium-bismuth dross removed. The residual calcium and magnesium in the lead are removed with chlorine or molten chlorides before casting as refined lead. The calcium-bismuth skims are treated with chlorine or molten chlorides for removal of calcium and magnesium. The crude bismuth is refined as outlined above.

Crystallization, by the Pattinson or Hall process, is not used today, except to supplement the chlorine refining of crude bismuth or in re-treating some of the products from dross and skims.

The Sperry process for production of white lead employs anodes of lead bullion, producing an anode slime which is treated for the recovery of silver, gold, and bismuth, as in the electrolytic refining of lead.

Current Production.—The current production of bismuth in the Western Hemisphere is estimated to be between 2,500,000 and 3,000,000 lb. per year. The principal producers are: the American Smelting & Refining Co., the Cerro de Pasco Copper Corp., the Consolidated Mining & Smelting Co. of Canada, Ltd., the International Smelting & Refining Co., the U. S. Smelting, Refining & Mining Co. The New York quotation for refined bismuth has been \$1.25 per pound since October, 1939.

Uses.—The principal use of bismuth for many years was in the production of pharmaceutical compounds. During the last ten years, however, the industrial and engineering uses of bismuth and its low-melting alloys have expanded rapidly. The addition of small amounts of bismuth and lead to some of the strong aluminum alloys is used to render the alloys free cutting. The addition of fractional percentages of bismuth to the so-called stainless steels and to the manganese steels improves the machinability of these steels.

Bismuth is a constituent of a number of eutectic alloys, some of which are:

Melting temperature		Composition				
°F.	°C.	Bi	Pb	Sn	Cd	Others
116.6	46.8	44.70	22.60	8.30	5.30	In 19.10
158.0	70.0	49.41	27.67	12.88	10.02	
196.7	91.5	51.65	40.20	8.15	
203.0	95.0	52.00	32.00	16.00		
216.5	102.5	53.90	25.90	20.20	
255.7	124.3	55.50	44.50			
266.0	130.0	56.00	40.00	Zn 4.00
281.3	138.5	57.00	43.00		
291.0	144.0	60.00	40.00	

The eutectic alloys are not satisfactory for many applications, because of their very narrow freezing ranges. Many alloys having wide freezing ranges have been developed. Some of the fusible alloys expand during solidification, some shrink, while others grow rapidly in the solid state after solidification. One alloy composed of bismuth, lead, tin, and cadmium shrinks during solidification; further shrinkage occurs on cooling from solidification temperature to room temperature, when it begins to grow. The growth is very rapid for about 10 to 12 hr. Approximately 95 per cent of the total growth occurs in the first 12 hr., and this growth almost exactly compensates for the shrinkages that occur during solidification and cooling of the alloy. The alloys that grow in the solid state are in general harder in the aged condition than when first cast.

Bismuth alloys are employed in:

- Safety plugs for compressed-gas cylinders and tanks.
- Fusible elements in automatic sprinkler heads, fire-door release links, automatic shut-offs for electric and gas water-heater systems.
- Constant-temperature baths for autoclaves.
- Liquid seals for bright-annealing and nitriding furnaces.
- Low-melting solders.
- Forming dies in aircraft construction.
- Spotting, erection, and checking fixtures for aircraft construction.
- Bending thin-wall tubing and molding.
- Production of accurate patterns.
- Cores on which copper, iron, and other metals are electroformed.
- Anchoring dies, punches, machine parts, magnets, and ceramic parts.
- Chucks for holding irregular or delicate articles during machining operations.
- Spray coating for wood patterns, core boxes, etc.
- Models for engraving machines.
- Proof casting of forging dies, plastic molds, and other irregular cavities.
- Selenium rectifiers.

CHAPTER VII

LEAD

BY R. G. BOWMAN¹

Nature and Uses.—Lead is the heaviest and softest of all the common metals. It has a specific gravity of 10.37 to 10.65 (molten); 11.35 to 11.37 (solid); it is, in its pure metallic state, so soft as to be readily scratched by the fingernail, while it easily marks paper with a gray streak. Only the pure metal exhibits this degree of softness, many commercial grades containing small amounts of antimony, arsenic, copper, and zinc being distinctly harder. The degree of hardness increases with the amount of impurity present. The metal has a dull bluish-gray color, is malleable but not ductile. Its tensile strength is low, 2600 to 3300 lb. per sq. in.; its elastic limit is 0.5 lb. The tensile strength is about two and one-half times the tenacity. Lead is not sufficiently ductile to be drawn into fine wire.

Lead melts at 327.4°C., boils at about 1525°C. (at 760 mm.), but does not readily distill. If, however, a mixture of zinc and lead is subjected to distillation at a high temperature, the zinc vapor carries over with it a considerable quantity of lead vapor; and hence the source of part of the losses in lead smelting. Lead is somewhat volatile when heated to a cherry red with access of air.

Commercial Grades of Lead.—The commercial grades of refined lead as established by the A.S.T.M. are shown in Table 1.

Uses of Lead.—Lead is used (1) in the form of refined metal, (2) as a base for alloys with other metals, (3) in the form of chemical compounds.

The proportion of lead consumed in various applications is shown in Table 2.

In smelting, lead is used as a collector for other metals, particularly for gold and silver, from which it is later separated, generally by use of zinc in the Parkes process of desilverization.

Lead alloys readily with most of the nonferrous metals and forms the base for a large number of important industrial alloys. The principal types of lead-base alloys are: type metal, bearing or babbitt metal, shot, solders, casting metals, leaded brasses, and fusible alloys used for the protection of electrical apparatus, in automatic sprinklers, etc. From 0.1 to 0.2 per cent arsenic is added to lead used in making shot to increase the hardness and sphericity of the product. Antimony imparts the quality of hardness essential to some ammunition and the property of expansion on solidification essential in type metal and casting metals generally. Bearing metals comprise alloys of lead and antimony, or these together with copper, tin, and zinc. The addition of lead to brass produces an alloy that is soft and machines easily. Solder is commonly an alloy of lead and tin; the melting point varies with the proportion of these constituents and others, sometimes added for special purposes. Commercial solder ranges in composition from 3 to 60 per cent tin, the remainder being lead. The alloy of 1 part tin and 3 parts lead melts at 452°F., tin alone melting at 442°F. With increase of tin content to 56 per cent the fusion point is lowered to 345°F., then rises to 352°F., with further increase to 75 per cent tin. In practice, therefore, solder

¹ General superintendent, International Smelting & Refining Co., East Chicago, Ind. In the preparation of this chapter the former chapter by Mr. G. C. Riddell was drawn upon freely. Figures 3, 4, 44-60, and 65 are from Vol. 121, *Trans. A.I.M.M.E.*, by permission.

seldom contains more than 50 per cent tin. The addition of bismuth, cadmium, or mercury lowers the melting point below the boiling point of water. The low-fusion-point alloys of this type have many commercial uses.

The most extensive single application of a lead-casting alloy is in the manufacture of storage-battery grids which are made of an alloy of 6 per cent antimony and 94 per cent lead.

Type metal has a wide range of composition, *e.g.*, 50 to 80 per cent lead, 2 to 35 per cent tin, and 5 to 30 per cent antimony. Some also contain nickel, copper, and bismuth.

TABLE 1.—STANDARD SPECIFICATIONS FOR PIG LEAD¹

Tentative specifications for pig lead published since 1919, and last revised in 1940 by the American Society for Testing Materials (A.S.T.M. Designation B 29-40) cover refined lead in pig form made from ore or other material by processes of reduction and refining, and exclude lead reclaimed by simple melting, dressing, and casting. The requirements as to chemical composition are as follows, in percentages:

	Corroding lead	Chemical lead	Acid lead	Copper lead	Common desilverized lead		Soft undesilverized lead
					A	B	
Silver, max.	0.0015	0.020	0.002	0.020	0.002	0.002	0.002
Silver, min.		0.002					
Copper, max.	0.0015	0.080	0.080	0.080	0.0025	0.0025	0.04
Copper, min.		0.040	0.040	0.040			
Silver and copper together, max.	0.0025						
Arsenic, max.	0.0015						
Antimony and tin together, max.	0.0095						
Arsenic, antimony, and tin together, max.		0.002	0.002	0.015	0.015	0.015	0.015
Zinc, max.	0.0015	0.001	0.001	0.002	0.002	0.002	0.002
Iron, max.	0.002	0.002	0.002	0.002	0.002	0.002	0.002
Bismuth, max.	0.05	0.005	0.025	0.10	0.15	0.25	0.005
Lead (by difference), min.	99.94	99.90	99.90	99.85	99.85	99.73	99.93

¹ American Bureau of Metal Statistics, 1941.

Corroding lead is a designation that has been used for many years in the trade to describe lead which has been refined to a high degree of purity.

Chemical lead has been used for many years in the trade to describe the undesilverized lead produced from Southeastern Missouri ores.

Acid lead is made by adding copper to fully refined lead.

Copper lead is made by adding copper to fully refined lead.

Common desilverized leads A and B are designations that are used to describe fully refined desilverized lead.

Soft undesilverized lead is used in the trade to describe the type of lead produced from ores of the Joplin, Mo., district.

One of the most valuable properties of lead is its resistance to corrosion, though its physical weakness is a disadvantage in many mechanical operations. The addition of comparatively small amounts of some other metals greatly increases its mechanical strength without impairing its corrosion resistance and other valuable characteristics.

TABLE 2.—USE OF LEAD IN THE UNITED STATES*
(In tons of 2000 lb.)

Purpose	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943
White lead.....	64,500	80,000	85,500	86,000	71,000	75,000	65,500	85,000	75,000	50,000
Red lead and litharge ^b	42,000	47,500	54,000	57,000	43,000	57,200	59,400	89,100	68,000	79,000
Storage batteries.....	163,000	175,000	191,000	192,000	107,000	198,000	220,200	245,000	215,000	257,000
Cable covering.....	35,200	38,900	41,400	90,000	60,000	74,400	107,400	173,000	165,000	132,000
Buildings.....	30,000	32,000	40,000	45,000	36,000	50,000	65,000	95,000	110,000	62,000
Automobiles.....	7,300	10,000	11,100	12,000	6,000	8,000	11,000	12,000	3,000	1,000
Ammunition.....	34,800	29,200	32,500	39,500	31,200	42,300	56,000	71,500	83,000	178,000
Terne plate.....	2,800	4,700	6,200	6,400	4,300	6,000	6,000	8,700	4,900	5,000
Foil.....	10,200	15,000	28,500	21,700	22,000	21,800	23,500	46,000	7,700	13,000
Bearing metal.....	12,100	13,000	10,500	15,000	9,000	12,800	14,000	25,000	20,000	23,000
Solder.....	16,000	20,000	22,000	22,000	15,000	20,000	24,000	38,000	38,000	38,000
Type metal.....	13,000	15,000	17,000	17,000	12,000	14,000	10,800	20,000	20,000	17,000
Calking.....	10,000	12,000	13,500	15,000	12,000	16,000	19,200	31,000	40,000	30,000
Castings.....	5,000	5,000	5,750	6,000	6,000	7,500	9,000	14,000	14,000	14,000
Other uses ^d	36,300	40,700	48,600	54,100	51,500	63,100	85,000	99,700	149,800	215,000
Totals.....	488,000	538,900	633,550	678,700	546,000	607,000	782,000	1,050,000	1,000,000	1,100,000

^a Includes antimonial lead.

^b Exclusive of oxides for storage batteries.

^c Under the head of building is included the lead used in chemical construction.

^d Among "other uses" the largest item in recent years has been the manufacture of lead tetraethyl for tempering gasoline. Also included are lead for brass making, collapsible tubes, lead-lined pipe, lead-headed nails, railway equipment, shipbuilding, and many miscellaneous uses. The figures for 1942-1943 include lead exported.

^e Included in "other uses."

NOTE: We estimate that about 75 per cent of the lead that goes into storage batteries returns into production of soft and hard lead, which production is not accounted for fully in the usual tables owing to omission of most of the secondary smelters. For this reason the totals in the above accounting are in excess of shipments reported ex-primary refineries.

In the accounting for the use of lead in 1941 the allocation to ammunition does not include the use for that purpose in the government arsenals, and also omitted are consignments of refined pig lead for governmental use otherwise. Table and notes by courtesy of American Bureau of Metal Statistics.

Commercial grades of lead containing such additions are not usually classed as alloys, owing to the small amount of metal other than lead.

The most important commercial grade of this type is that containing 0.04 to 0.06 per cent copper, which is widely used for protective sheathing on electric cables and for chemical-plant equipment. Other important grades are tellurium lead, containing about 0.05 per cent tellurium, and calcium lead, containing 0.02 to 0.05 per cent calcium.

The addition to steel of up to 0.50 per cent lead produces an important increase in machinability.

Alloys of Lead.—The compositions of some of the leading industrial alloys of lead are given in Table 3.

The largest use of lead in the form of a chemical compound is in the field of pigments. The most important of these is white lead, a basic carbonate, $2PbCO_3 \cdot Pb(OH)_2$, used alone or as a base for mixed paint. Red lead, Pb_3O_4 , is used as a rust-inhibitive priming coat for iron or steel. Lead basic sulphate, known as sublimed white lead, and lead chromate are also important lead pigments.

Litharge, PbO , is used in large amounts in the manufacture of storage batteries, in rubber compounding, and in the manufacture of glass and ceramic glazes. Lead borate is used in ceramics; lead arsenate is an insecticide; and lead acetate and other compounds are used in medicine.

History.—Lead is one of the six so-called prehistoric metals. The oldest people of whom there is any record, the Egyptians, used lead in glazing pottery, and the abundance of silver among the ancients must have been derived from argentiferous lead ores in various places. Among the Egyptians, gold, silver, and lead came into use, together, in the period 7000 to 5000 B.C. One of the oldest pieces of lead in existence is a figure in the British Museum which antedates 3800 B.C. Lead was known and used by the Chinese before 3000 B.C. The Phoenicians worked the Rio Tinto deposit about 2000 B.C. The mines at Laurium, Greece, reopened by a French company in 1863, flourished in the fifth century B.C. In the third century B.C. the Romans operated the lead mines in Spain, the same deposits that today form one of the major districts of the world.

About the period A.D. 700 to 1000, the German lead-silver mines in the vicinity of the Rhine and the Hartz Mountains were opened, and in A.D. 1200 those in Saxony, Silesia, and Bohemia. Lead mining in the United States, now the leading producing country of the world, dates back to the beginning of the seventeenth century (1621) when lead was mined and smelted in Virginia. The lead ores of the United States came from the Mississippi Valley between 1700 and 1867, in which latter year the first great mines of the West were opened. The Mississippi Valley ores are non-argentiferous, i.e., they do not contain enough silver to pay for its extraction. The ores of the Western states are argentiferous and in most instances are quite complex in composition.

The manner in which prehistoric people extracted lead from ore is unknown, but it is readily imagined that primitive furnaces, small pits dug in the ground or in the hillsides, enclosed by stones to form a small shaft, provided early equipment for the recovery of lead from oxide and sulphide ores heated with charcoal. Blast, to produce the temperature required for forming slag, must have been applied by reed and bellows. The furnaces found in Sinai in which copper ores were smelted about 4000 B.C. had this form: a cavity 30 in. deep, a side wall 26 in. high, and with two tuyère openings; the furnaces at Laurium were similar. At Bawdwin, Burma, the remains of the ancient lead-silver smelting and refining furnaces show this same crude Scotch-hearth effect. These Burma furnaces have no iron work of any kind in or around them. They are simply an excavation in the side of the hill, semicircular in horizontal cross-

section; the radius at the top is 2 ft., tapering to about 9 in. at the sump. The depth from the top edge of the furnace to the bottom of the sump is between 5 and 6 in. Back of the clay lining of the sides are three 3-in. square air passages extending from the top edge to the level of top of sump. The operation of these primitive furnaces was undoubtedly similar to that followed in the modern Scotch hearth. Similar contrivances, the log furnace and the ash furnace, were used in smelting ores in the

TABLE 3.—LEAD-BASE ALLOYS

Name	Pb	Sb	Sn	
Type metal:				
Best.....	50	25	25	
German.....	75	23	2	
Common.....	70	18	10	Cu, 2
French.....	60	30	10	
Linotype (American).....	55	30	15	
Bullets (shrapnel).....	85	12	3	
Engraving plate.....	94	6		
Pewter:	60	40		
Usual.....	20	80		
French.....	18	82		
Bearing metal:				
Atlantic Coast Line.....	85	15		
Pennsylvania R.R.....	87	13		
Baltimore & Ohio R.R.....				
Thin linings.....	94-96	3-5	0.5-1.5	
Thick linings.....	86	10-12	3-5	
Chicago & Eastern R.R.....	84-85	12-14	2	
Chesapeake & Ohio R.R.....	91.5	7	1.5	
Magnolia metal.....	79.75	15	5	Bi, 0.25
Solder:				
No. 1, tinman's.....	34		66	
No. 2, half and half.....	50		50	
No. 3, plumbers'.....	66		34	
Cable sheathing ^a	98.0		2.0	
	99.2		0.8	
Frary metal (Ulco).....	97+			{ Ca 1 Ba 2
White metal, or antifricition bearings:				
Heavy load.....	87	7	6	
Jacoby metal.....	85	10	5	
Jacoby metal.....	62	10	27	
French R.R. (Cie. de l'Est).....	80	8	12	
French R.R. (P.-L.-M. R.R.).....	70	10	20	
Ship shaft bearing.....	72	7	21	
Shot.....	99.5-99.8			As, 0.2-0.5
Terne metal.....	80.25	1.75	18	

^a Special leads used for cable sheathing contain Cu, Sb, or Ca in amounts less than 0.10 per cent and are not ordinarily classed as alloys. The most important one of these contains 99.85 per cent Pb and 0.06 per cent Cu.

Mississippi Valley about 1720. In 1836 the first Scotch hearth was erected in this country. This furnace had been in operation in England since 1730.

Chemical Properties.—Lead is tetravalent; its atomic weight is 207. It tarnishes rapidly in moist atmosphere, although its surface undergoes no change in perfectly dry air, or in water that is free from air. If melted in contact with air, it oxidizes, with a coating of iridescent pellicles of suboxide which, at dull red heat, are converted into PbO. If the heating is continued at a temperature of 400 to 430°C., the PbO gradually changes to red oxide (Pb₂O₄), which dissociates into 3PbO and O at 550°C. The other oxides that lead forms are the sesquioxide, Pb₂O₃, and the peroxide, PbO₂. All oxides with more O than PbO are decomposed into PbO and O at 630°C.

The best solvent of lead is nitric acid, the very dilute acid acting more rapidly than the strong. Dilute hydrochloric and sulphuric acid have little effect on lead, these acids forming coatings of PbCl₂ and PbSO₄ which protect it further from action. Up to 200°C.—the highest temperature employed under normal conditions in acid concentrating practice—pure lead is but little attacked by strong HCl or by the pure or nitrous sulphuric acid, but above 200° the action becomes stronger, and at 260°C. lead is completely dissolved. Boiling concentrated HCl and H₂SO₄ attack the metal slowly, even in large masses, and dissolve it with fair rapidity if it is in a finely divided condition. Nitrous sulphuric acid acts upon lead at all temperatures more readily than does the pure acid. Acetic, citric, tartaric, and other organic acids act upon it slowly in contact with moist air. It is attacked by SO₂ between 550 and 850°C., and is also acted upon by HF, but the dissolution in hydrofluoric acid is quickly checked by the formation of PbF₂; hence the acid can be stored in lead vessels.

The compounds of lead are poisonous practically in proportion to their solubility; the metal itself and its sulphide, being incapable of absorption as such into the system, are almost innocuous, while the soluble salts, chloride, nitrate, acetate, etc., are active irritant poisons. The oxide, sulphate, and carbonate are less active, but continued exposure to lead fume, or to any atmosphere in which these substances are present in the form of dust, is dangerous and will result in lead absorption or "plumbism." This condition is entirely curable and can be entirely prevented by adequate ventilation of working places, the use of respirators, protective clothing, and personal cleanliness. By reason of such measures and careful medical inspection, modern lead industries offer no greater hazards to the worker than do most other industrial fields.

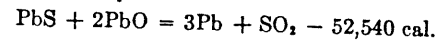
Lead Compounds.—The more important compounds of lead and the chemical reactions that are of importance in the extraction of the metal are as follows:

Lead Oxide, PbO.—This is the oxide of greatest metallurgical importance. It occurs in two forms—massicot and litharge. Massicot is an amorphous yellow powder produced by heating lead on flat hearths at a full red heat, continually removing the film of suboxide, and oxidizing it to the yellow oxide at a low temperature, avoiding fusion. On raising the temperature to a bright red heat, this oxide melts and, on cooling, solidifies as crystalline litharge. Litharge is obtained on a commercial scale by cupeling refined lead and collecting the oxide as a skimming or a fume. The melting point of litharge is 883°C.; it is volatile in air below 900°C. It is a good conductor of electricity when molten.

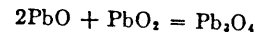
Toward acid furnace materials, litharge is a strong base, quickly corroding them by forming lead silicates. It is an excellent flux, forming fusible compounds with oxides that are infusible alone, such as CaO, BaO, MgO, and Al₂O₃. These bases do not always enter into chemical combinations with PbO, but are simply held in fused solutions by an excess of litharge. In the case of the metallic oxide CuO, 1 part of CuO forms a fusible mixture with 1.8 part of PbO. No chemical compound occurs, but there is a eutectic with 32 per cent CuO freezing at 689°C. This explains the

fact that, in cupeling, coppery litharge flows more readily than litharge free from copper. Litharge readily gives up its oxygen. Sulphur, tellurium, arsenic, antimony, tin, copper, zinc, and iron are wholly or partly oxidized when melted with litharge, the oxides being either volatilized or slagged by the surplus of litharge.

Reduction of PbO by carbon begins at 400 to 500° and is vigorous at 700°C. Reduction by carbon monoxide begins at 160°, by hydrogen at 235°C. Heated to bright redness with lead sulphide, in the proportion of two molecules of litharge to one of sulphide, all the lead in both compounds is reduced to metal, and sulphur dioxide is evolved, according to the equation



Minium or Red Lead, Pb₃O₄.—This is a combination of 2PbO and PbO₂, a bright red powder prepared by heating a mixture of PbO₂ and PbO at about 250°C



Lead Peroxide, PbO₂.—This is a powerful oxidizing agent, detonating with phosphorus. It is used in the manufacture of matches and in storage batteries, in which latter it is repeatedly destroyed and reformed during the operation of discharging and recharging.

Lead Carbonate, PbCO₃, and White Lead, 2PbCO₃.Pb(OH)₂.—Lead carbonate occurs in nature as cerussite. At 200°C. it decomposes into PbO and CO₂, and at the same temperature is reduced to metallic lead by CO. The white lead of commerce is a hydrated basic carbonate. This pigment has for centuries been prepared by the "Dutch" or "corroding" process which, briefly stated, consists in the slow corrosion of lead by the vapor of acetic acid and the conversion of the corroded material into hydrated carbonate of lead by CO₂ generated from decomposing organic matter. The process is tedious, taking over 90 days to complete. The lead is cast into "buckles," which, exposing maximum surface to corrosion, are placed in clay pots containing dilute acetic acid or vinegar. The pots are stacked in tiers and covered with tanbark. The carbon dioxide required for the ultimate conversion of the corroded lead is generated by the fermentation of the bark. The white carbonate is cleaned from the buckles in revolving drums and the impurities are separated by flotation, washing and screening before it is dried and packed for shipment or is ground in oil for use. From 125 to 129 lb. of white lead should be obtained from 100 lb. of metal.

A considerable proportion of white lead is still produced by this process, which gives an excellent pigment. More modern processes reduce the time required, afford better opportunities for control of the composition and physical characteristics of the product, and yield a product that requires no further purification. The principal processes in use are the following:

Carter Process.—Finely divided metallic lead is treated with acetic acid and carbon dioxide in revolving wooden drums. The lead is completely converted into basic carbonate in 8 to 12 days and is washed, dried, and pulverized.

Euston Process.—Metallic lead is dissolved in acetic acid as basic lead acetate and precipitated as basic carbonate with carbon dioxide.

Sperry Electrolytic Process.—Pure basic carbonate of lead is produced in a bifluid electrolytic cell having a lead anode and a steel cathode, separated by a linen diaphragm. The two electrolytes are sodium acetate solutions differing in carbonate-ion concentration. The lead dissolves at the anode, is reprecipitated as basic carbonate in suspension in the anolyte, and flows continuously from the cell in this suspension as the anolyte is circulated. It is removed by settling and filtration and is dried, pulverized, and packed. The catholyte acts as a feeder to maintain an exact concentration of the anolyte through electrolytic control. The purity of the

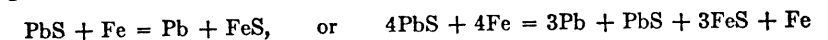
product is independent of the purity of the anode lead, since only the lead dissolves. The process affords an opportunity for complete control of the composition and physical characteristics of the product at all times and produces an extremely pure and brilliantly white pigment.

Sublimed White Lead (Basic Lead Sulphate).—This is a white pigment, ranging in composition from pure 2PbSO₄.PbO to 75 per cent PbSO₄, 20 per cent PbO, and 5 per cent ZnO and is largely produced directly from lead ore, whereas the basic carbonate (white lead) is made almost exclusively from metal. Basic lead sulphate is used extensively in paint and in the manufacture of oilcloth, paper, and rubber goods. The raw material used in its manufacture is silver-free galena from the Missouri field. This is ground fine, mixed with carbon (and gray slag from the ore hearth), and smelted in an oxidizing atmosphere. The pigment is collected in baghouses. Blue fume, or "sublimed blue lead," is a by-product of the process and is used in the same industries as is the major product. Sublimed blue lead consists of 50 to 53 per cent PbSO₄, 41 to 38 per cent PbO, with small proportions of PbS, PbSO₄, ZnO, and carbon.

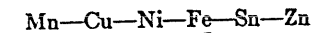
Lead Silicates.—Lead silicates are much used for glazing tile, pottery, etc. Lead oxide and silica begin to combine at the softening temperature of the oxide, i.e., below 800°C. The silicates do not give up their lead readily, the ordinary reducing agents sulphur and carbon decomposing them with difficulty. Iron in excess effects the decomposition of lead silicates at bright-red heat, forming monosilicates (2FeO.SiO₂). FeS throws down some Pb, a double silicate of lead and iron being the result.

Lead Sulphide, PbS.—This occurs in nature, as galena, and can be artificially prepared by melting sulphur and lead, or by adding hydrogen sulphide to a solution of a lead salt. It is produced in smelting lead ores as a sublimate on the cooler part of the furnace walls. PbS melts at about 1120°C. to a thin fluid which penetrates the firebrick of the furnace; furnace linings usually contain a network of crystalline galena. It volatilizes at temperatures below its melting point. Sublimed galena constitutes a large portion of the accretions on the shaft walls of lead blast furnaces.

Being isomorphous with Ag₂S, Cu₂S, ZnS, FeS, etc., lead sulphide readily mixes with these sulphides in all proportions, forming the mattes obtained in smelting complex sulphide ores. Galena is decomposed by fusion with iron, the reaction forming the basis of what is known as the "precipitation" process of lead smelting.



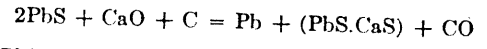
Lead sulphide is decomposed by those metallic elements which have a stronger affinity for sulphur than lead, in the following order:



manganese forming the strongest and lead the weakest sulphide. In the smelting of lead ores, manganese does not have to be considered in this connection, as it is usually present as MnO₂, which enters the slag and hence is found only in small amount in the matte.

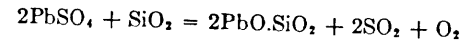
In smelting practice, the decomposition of PbS is never complete. It is customary to calculate the iron necessary for the decomposition of PbS in accordance with the formula $\text{Fe} + \text{PbS} = \text{Pb} + \text{FeS}$; if less iron is added, the resulting matte remains too rich in lead, while if an excess is supplied it simply goes into solution in the PbS-FeS matte. An excess of iron in the charge, while often advantageous in cutting out crucible crusts, may be disadvantageous in decomposing argentiferous galena, since, owing to the affinity of Ag₂S and FeS, more silver will be drawn into the matte than can be accounted for by the amount of lead present. In addition to having the correct amount of iron present to decompose PbS, it is important to have the temperature as high as possible, within reasonable limits.

A basic ferrous silicate, $4\text{FeO}\cdot\text{SiO}_2$, will decompose PbS readily; the single silicate, $2\text{FeO}\cdot\text{SiO}_2$, has little effect. CaO and BaO have, in the presence of carbon, a decomposing action on PbS .



Lead Sulphate, PbSO_4 .—This occurs in nature as anglesite and is formed in roasting PbS and in precipitating lead salts with H_2SO_4 . It is the most stable of all sulphates of the heavy metals, remaining unaltered at a bright-red heat. At 800 to 1000°C., it dissociates, fusion also occurring between 950 and 1000°C.

Silica decomposes PbSO_4 at 1030°C. in accordance with the equation

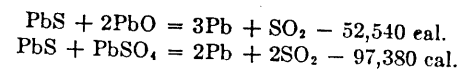


this reaction being the basis of "slag roasting." This decomposition by silica is governed by the viscosity of the lead silicates formed, the viscous slag enveloping PbSO_4 and blocking the action. According to Mostowitsch, the most rapid decomposition and the lowest loss of lead by volatilization lies between the singulo- and bisilicate containing 10 to 15 per cent SiO_2 .

Fe_2O_3 also has a decomposing effect on PbSO_4 , though in less degree than SiO_2 . FeO , above 800°C., is oxidized by some of the O from PbSO_4 . Iron at high temperature is both oxidized and sulphurized: $4\text{Fe} + \text{PbSO}_4 = \text{Fe}_2\text{O}_3 + \text{FeS} + \text{Pb}$; calcium is sulphatized: $\text{CaO} + \text{PbSO}_4 = \text{CaSO}_4 + \text{PbO}$; and metallic lead is oxidized: $\text{Pb} + \text{PbSO}_4 = 2\text{PbO} + \text{SO}_2$.

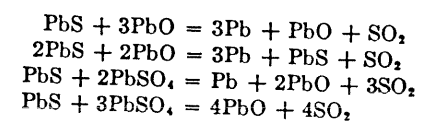
Carbon and carbon monoxide reduce lead sulphate to PbS , with the formation, also, of Pb and SO_2 . This double reaction explains the disappearance of S as SO_2 in the reducing fusion of a lead blast furnace. In smelting the gray slag from the ore hearth, as much as 50 per cent of the sulphur is usually expelled.

Reactions between Lead Oxide, Sulphide and Sulphate.—Intimate mixtures of PbS and PbO , and of PbS and PbSO_4 , such as exist in the roasting and smelting of lead ores, react in accordance with the following equations to form metallic lead and SO_2 :



These two equations form the basis of the roasting and reaction or air-reduction process. Except for the fact that the gaseous product SO_2 is withdrawn from the furnace as fast as formed, both these reactions would reverse and equilibrium result.

If there is an excess of PbS or PbO over that called for by the equation, the excess remains unaltered. If there is an excess of PbSO_4 , part or all of the lead is obtained as PbO .



Plumbites and Plumbates.—The oxides PbO and PbO_2 form plumbites and plumbates with alkali, alkali earths, and some metallic oxides. The orthoplumbate, Ca_2PbO_4 , occurs in the blast roasting of lead sulphides with lime diluents.

Lead Ferrite.—The fact that in the crucible assay for lead the presence of Fe_2O_3 acts unfavorably on the yields of lead is believed due, in part at least, to the formation of ferrite compounds, one of these having the formula $\text{PbO}\cdot\text{FeO}\cdot 4\text{Fe}_2\text{O}_3$. The melting point of PbO is lowered 133°C. by the addition of 12 per cent by weight of Fe_2O_3 .

Lead Chloride.—This is formed by the action of chlorine upon lead and in a chloridizing roast of lead and its compounds. The volatility of PbCl_2 is the basis of a process

for the extraction of lead from its ores, the chloride volatilization process, in which the chloride fume is precipitated by being passed through an electrostatic precipitator. The solubility of PbCl_2 in saturated sodium chloride liquor is also the basis of another process of lead recovery, the brine-leaching process, in which sulphide ores roasted in contact with sodium chloride are dissolved by strong brine solutions, out of which the lead is precipitated either electrolytically or on scrap and sponge iron.

Lead Selenide and Telluride (PbSe and PbTe).—These occur as clausthalite and altaite and are formed by the direct union of components. They are readily decomposed by roasting. Selenides and tellurides are found in the anode mud formed in the electrolytic refining of copper and lead, this mud being the raw material for the production of selenium. Te Pb
Te Se

Lead Borates.—Lead oxide and boric trioxide melt together in all proportions, and the compounds formed are more fusible than the corresponding silicates. Advantage is taken of this fact in lead and silver assaying by the use of borax as a flux. Lead borates are used in the preparation of ceramic glazes.

Lead Fluosilicate, PbSiF_6 .—This is formed by the action of H_2SiF_6 on PbO when some SiO_2 is precipitated. A solution containing about 8 per cent PbSiF_6 and 11 per cent free H_2SiF_6 is used as electrolyte in the electrolytic refining of lead.

Lead Ores.—Lead and zinc are commonly associated in mineral deposits, sometimes intimately mixed, sometimes sufficiently segregated so that one metal predominates, but seldom free entirely from the other. The geological and geographical distribution of the two metals is, therefore, nearly identical.

All lead ores contain substances other than lead minerals. Some of these substances (e.g., gold, silver, or copper) can be recovered in the smelting process and may add much to the value of the ore. The common impurities in lead ores are silica, iron, lime, barytes, zinc, antimony, and arsenic. The first three (in minor amounts) may be beneficial or detrimental in any given ore, depending upon whether the bulk of the ore supply of the smelter carries an excess of one or the other of these elements which, in proper proportions, are required in the smelting operation. On the other hand, zinc and, to a less extent, antimony are always detrimental and detract from the value of the ore unless separated from the lead before shipment to the smelter. Sulphur, a constituent element of galena, is not considered a deleterious element except that carbonate ores of similar grade are more valuable, since they are cheaper to smelt. Barytes and other less common constituents of lead ores, including traces of valuable metals (bismuth, cadmium and rare elements), are seldom present in quantities sufficient to affect the value of the ore to the miner.

The more common ore minerals of lead are the following:

Mineral	Formula	Percentage of lead
Galena.....	PbS	86.4
Cerussite.....	PbCO_3	77.5
Anglesite.....	PbSO_4	68.3
Pyromorphite.....	$3\text{Pb}_2\text{P}_2\text{O}_8\cdot\text{PbCl}_2$	76.3
Wulfenite.....	PbMoO_4	56.3
Jamesonite.....	PbSb_2S_6	34.1

Galena is the most common and important of these minerals. The next three minerals in the list usually result from the surficial oxidation of galena, the sulphate being usually an intermediate stage in the oxidation to the carbonate. Pyromorphite

and wulfenite are of minor importance. Jamesonite is considered more an ore of antimony than of lead.

Sphalerite weathers more readily than galena and zinc, therefore it is often carried below water level more rapidly and completely than lead. This fact accounts for some mines changing from predominantly lead mines to zinc mines with greater depth. Apart from the effect of such secondary enrichment, this change is often encountered in primary ores with increase in depth.

Important types of lead deposits are as follows:

1. Deposits formed at shallow depth in sedimentary rocks without apparent connection with igneous rocks. These have evidently formed under conditions of temperature and pressure approximating those of the present surface. They occur as tabular replacements of receptive strata usually in limestones and dolomites, but sometimes in quartzites or cherts and conformable with the enclosing strata; also as irregular masses along faults, in zones of brecciation, in fissures, joints, crevices, and cavities erratically distributed in the same rocks.

In regions of slightly disturbed strata the ore shoots tend to follow pitching troughs. The ores of this type usually contain lead (galena), zinc (sphalerite), and iron (pyrite) minerals; often manganese and cadmium; sometimes cobalt and nickel; but seldom gold, silver, copper, or antimony.

The deposits of this type are of worldwide distribution and are often extensive and commercially important. Their greater purity and simplicity of treatment, particularly of the ores in their oxidized zones, caused them to be exploited first and most extensively and to be the dominant factor in the world production of lead at one time. To this type belong, besides many others, the deposits of the Mississippi Valley and Silesia, between them producing 12 per cent of the world's production in 1940.

2. Deposits formed at shallow or intermediate depths genetically associated with igneous rocks, characterized by complex ores and comprising (a) vein deposits apparently formed near the surface, (b) veins filled under conditions of intermediate temperature and pressure, (c) disseminated pyritic replacements of igneous rocks, (d) silver-lead replacements in limestone.

Gradations between all these types are found, and many districts have related ore bodies of more than one of these types, sometimes examples of all of them.

With subtype 2a are classed certain deposits apparently formed near the surface in genetic connection with igneous rocks and usually occurring as veins, but sometimes as stock works and pipes in volcanic rocks and adjacent sedimentaries, also as replacements in sedimentaries with associated small contact metamorphic masses near igneous contacts. The deposits are usually worked primarily for gold and silver, but small percentages of galena, tetrahedrite, and sphalerite are usually present. The gangue is largely quartz, but adularia, calcite, rhodochrosite, rhodonite, barite, fluorite, and pyrite are often present, and the presence of minerals containing arsenic, antimony, bismuth, tellurium, selenium, and rarely tungsten and molybdenum is characteristic. Successive stages of mineralization are often evident, and secondary enrichment and alteration by descending waters have disguised some deposits.

The ores of the types 2b and c are usually complex, comprising much of the same minerals of zinc, lead, copper, iron, gold, and silver, and often arsenic, antimony, bismuth, and other metals. In subtype 2d, the silver-lead deposits in limestone, zinc is apparently a minor factor, but often when followed to depth, zinc replaces lead as the predominant metal. Many zinc mines are exhausted silver-lead mines.

To subtype 2a belong the deposits of the San Juan region and Lake City in Colorado, the Schemnitz deposits in Hungary, the Mapimi and Santa Eulalia deposits in Mexico, and the deposits of Insbach and Freiberg in Germany; to subtype 2b belong the

deposits of Coeur d'Alene, Idaho; and to subtype 2c belong those of Bawdwin, Burma, and Ridder, Siberia. Subtype 2d comprises the deposits of Leadville, Colo., Park City, Utah, and Sierra Mojada, Mexico. The importance of the ores derived from the deposits of the first three subtypes is due largely to smelting practice based on the use of lead as a collector of the precious metals.

3. Deposits in veins originating at high temperature and pressure, in, or associated genetically with, igneous rocks. The ore minerals are blende, galena, pyrite, or pyrrhotite, quartz, calcite, garnet, rhodonite, etc. To this type belong the important deposits at Broken Hill, New South Wales, Australia.

4. Igneous metamorphic deposits containing minerals characteristic of contact metamorphism. The ore minerals are galena and its oxidation products (cerussite and anglesite), blende, smithsonite, calamine, and a gangue of calcite, rhodonite, garnet, pyroxene, hornblende, magnetite, and tremolite. Among the deposits of this type are those of Magdalena, N. M., and the Horn Silver mine, Utah, occurring on or near contacts of limestone with igneous rocks.

Recovery of Lead from Ores.—Metallic lead has been recovered commercially from its ores almost exclusively by smelting in carbon-heated furnaces—either blast or ore hearth. Electric furnaces have been used for complex-ore reduction, but have not become of practical utility, and it would seem that no great promise of development exists in this direction as far as lead is concerned, owing to the high volatility of lead compounds at the operating temperatures obtained in electric-furnace work.

Various processes intended to make available ores of low grade, or complex ores of lead and zinc, have received considerable experimental attention, and a number of commercial plants have gone into operation in the past using hydrometallurgical processes. Among these, the brine-leaching method and the chloride volatilization processes are by far the most important, the former in the field of zinc-lead sulphide and oxide ore, and the latter more particularly in the field of oxidized and semi-oxidized and sulphide ores of copper, lead, zinc, and silver.

The hydrometallurgical treatment of lead ore has been developed to the point where it can compete economically with concentration and blast-furnace smelting on some sulphide ores. The net recovery with concentration and smelting is approximately 85 to 90 per cent; leaching, with or without roasting, will sometimes recover 95 per cent. The mills and smelters already in existence will doubtless continue to operate, but the economic warrant for the erection of smelters may need to be more carefully considered in the future. In general, lead can be produced, at the present time, more cheaply by smelting than by leaching, if the material to be treated contains over 12 per cent of lead. Improvements in concentration have removed some of the former advantages offered by leaching processes, and at the present time their field of application appears to be limited to those low-grade ores which are not amenable to concentration to a point that will make smelting profitable.

Brine-Leaching Methods.—These involve the roasting (sulphating or chloridizing) of the sulphide, solution of the stable lead-silver compounds in acid brines, and the final recovery of the lead by electrolysis or, less frequently, by precipitation on scrap and sponge irons. The free sulphuric acid in the leaching solution limits the solution of the lead; when an average of 8 lb. of metallic lead per ton of mill solution has been precipitated, the same weakened solution can be returned and will dissolve more lead.

An interesting plant, using the Tainton process of brine leaching, went into operation in 1923 in Idaho, the result of extensive experimenting for several years by the Bunker Hill and Sullivan Co. While this plant is not now operating, it is described as an interesting and typical example of lead hydrometallurgy which may find some application in the future. In general, the Tainton process involves the roasting of galena to sulphate in an electrically heated rotary cylinder, at 500°C.;

the removal of soluble sulphates of manganese, magnesium, and other metals by water wash; the solution of lead sulphate in a brine that is saturated with salt and

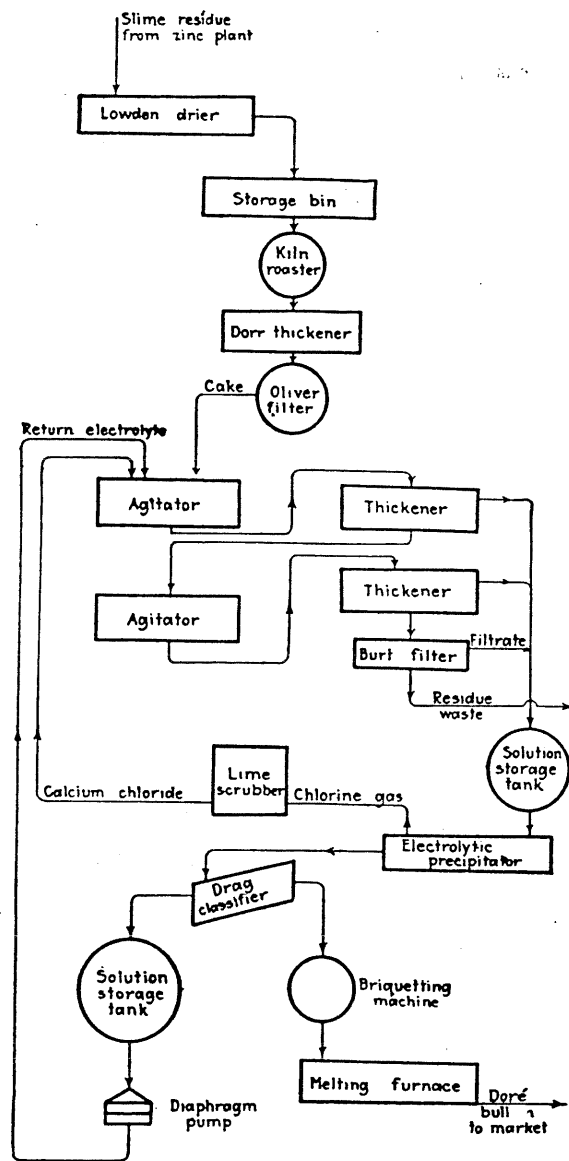


Fig. 1.—Flow sheet, Tainton process.

contains dissolved chlorine from the electrolytic cells; and the precipitation by electrolysis, with high current density and high acid strength, of lead and silver in a cell with rotating sheet-iron cathodes and graphite anodes. The sponge lead recovered

is thrown off the cathode by centrifugal force and floats out of the cell with the brine, or settles at the bottom of the cell, and is pressed into cakes for melting. A 95 per cent extraction of the silver and a 95 to 98 per cent extraction of the lead is possible. The process was developed for application to tailing from lead concentration and from electrolytic zinc production.

The preliminary roasting of the galena is a simple low-temperature sulphating roast (400 to 500°C.), without chloridizing, and the solution of the lead is made possible by the presence of dissolved chlorine in the brine. Ordinarily, and in the majority of other brine-leaching plants, a chloridizing roast is utilized to convert the lead sulphide into soluble chloride form.

Electrolytic-zinc plant tailings, lead sulphate flue dust, lead sulphate sludges from sulphuric acid chambers, oxidized ores of lead containing carbonate or sulphate, concentrating-mill tailing containing lead and silver sulphides, and complex zinc-lead-iron-sulphide ores comprise the products to which brine leaching is adapted.

In similar processes brines, containing dilute hydrochloric acid and also sulphuric acid, are applied in some cases directly to the raw sulphide ore, attacking the galena and leaving the zinc sulphide largely untouched.

The features of the treatment of an ore by such a process are the leaching by agitation of the unroasted ore in a hot brine solution containing a small quantity of hydrochloric acid; filtration and washing with hot weak solution and water; precipitation of the silver by means of lead in some form; precipitation of the lead by cooling the pregnant solution; and reduction of the lead by melting with a mixture of lime and coal dust. The solutions are circulated through spray heaters for re-use. The lead precipitation is based on the fact that a hot liquor at 90°C. will hold 8 to 10 per cent lead, whereas when cooled to 30°C., only 1 per cent will remain in solution.

In another similar process the chloridizing roast is eliminated. When ground very fine, galena will dissolve in a hot saturated and acidulated brine.

Brines carrying ferric chloride are adapted to removing silver, copper, and lead from complex sulphide ores, and have been used in many processes. Ferric brines are more widely used for leaching prepared ore than for attacking raw ores. Chloridized lead can be dissolved in a neutral brine; the silver is so easily precipitated from the solution on such substances as zinc sulphide that almost invariably the brine must also contain small amounts of acid or of ferric chloride or cupric chloride, all of which tend to redissolve any precipitated silver sulphide. A practical method for removing lead and silver from zinc sulphide, developed in Australia, consists of mixing the ore with sufficient zinc chloride to supply 33 per cent excess chlorine over that necessary for combining with the lead, silver, arsenic, antimony, and tin in the ore, and heating to 400 to 500°, out of contact with air. Chlorides of antimony, arsenic, and tin are volatilized, and chlorides of silver and lead remain in the anhydrous mass. These are leached in brine containing hydrochloric acid and ferric chloride.

Chloride Volatilization Processes.—These processes involve the chloridizing roast of the ore and the precipitation of the fume so produced by electrostatic precipitators. Except for the limitation of fume recovery to electrical apparatus, chloride-volatilizing methods are, in general, adapted to a wider range of ore and are less sensitive to trouble than the brine-leaching processes. Metallic-chloride vapors condense as colloidal particles of fume, each surrounded by an adsorbed film of air or gas, which prevents collection by any means other than electrical precipitation. Such particles pass untouched through water and most scrubbing devices, but are efficiently collected in the electrostatic precipitator. Baghouses will make a high recovery, but the corrosive action of the fume rapidly destroys the filtering fabric, and the fact that most such chloride mixtures are hygroscopic causes the precipitated fume to blind the fabric and render the baghouse ineffective.

*NaCl
HCl
H2SO4
Brine
ZnCl2*

*NaCl
FeCl*

*Lotrell
PAT*

The application of chlorine in lead metallurgy is important and is discussed elsewhere in the present volume.

Smelting Processes.—The smelting of lead ores is based on three principles: (1) the reduction of lead oxide by carbon or carbon monoxide; (2) the reaction between lead sulphide and lead sulphate or oxide, resulting in a double decomposition with the formation of lead and sulphur dioxide; and (3) the decomposition of lead sulphide by metallic iron. All these three reactions are endothermic, *i.e.*, they require heat supplied extraneously.

1. The first principle is the basis of what is known as the roast-reduction (or blast-furnace) method of smelting, in which lead oxide, lead silicate, or other oxidized compounds must first be prepared from sulphide ore by a roasting operation.

2. The second is what is known as the roast-reaction or air-reduction method—the basis of reverberatory and ore-hearth smelting.

3. The third is the basis of the precipitation method.

All these methods are employed commercially in the United States at the present time, either alone or in combination, the latter being more commonly the case. In practice, the principles are not so distinct as theoretically stated, the reactions fundamental to one process invariably play a certain part in the other processes.

If a lead ore were absolutely pure, there would be no other consideration in the smelting processes than those reactions which relate to lead and its chemical combinations. Practically, lead ores are never pure, the valuable minerals being mixed with a certain proportion of foreign matter, which must be separated by the formation of a slag. In the roast-reaction method of smelting, no slag, properly speaking, need be made, the molten reduced lead being liquated out from the impurities. However, the latter will still retain a high percentage of lead, and in order to effect a high degree of extraction from the ores, they must be subjected to a further smelting process in which a true slag is made. In making a slag, the object is to combine the impurities into a fusible silicate, which, when molten, will be of comparatively low specific gravity, in order that the heavier lead will settle to the bottom of the crucible of the furnace where it may be drawn off separately while the lighter slag will float on top. In addition to the slag and metal, there is formed, usually, a third substance, matte, which is lighter than the metal but heavier than the slag. Under certain circumstances, a fourth substance is formed which is called speiss; this is lighter than the metal but heavier than the matte and, therefore, forms a molten layer between the two. Matte is an artificial sulphide, consisting in lead smelting of the sulphides of iron, lead, and copper. It owes its origin to the incomplete elimination of sulphur from the ore, but is formed intentionally in lead smelting as a means of removing the copper as a separate product. Speiss is formed as the result of the presence of arsenic or antimony in the furnace charge. It usually approaches iron arsenide or antimonide in composition and acts as a collector for other metals such as nickel and cobalt.

The difference between lead smelting in principle and in practice is chiefly due to the incompleteness with which the basic reactions are carried out and the qualifying effect of the impurities that are commonly met with in ores. Thus certain metallic impurities are reduced with the lead, contaminating it and necessitating a subsequent refining process. Other impurities affect the composition of desirable slags. Others affect the running of the furnace in various ways.

If the ores are free from silver, the lead resulting from the smelting process is usually market grade after it has undergone a slight purification by liquating and cooling. To a limited extent the so-called silver-free (Mississippi Valley) lead undergoes treatment by the Parkes desilverizing process, as the amount of total impurities present is considerably reduced, and the price received as a premium for the better grade of lead and the small amount of silver recovered makes the operation profitable.

If the ore is argentiferous, as is the case with practically all districts outside the Mississippi Valley, the silver passes, for the most part, into the lead bullion, and the latter is then desilverized by either the Parkes or the electrolytic process.

The smelting of lead ores is carried on in three types of furnaces: the reverberatory, the ore hearth, and the blast furnace. Of these, the first has become almost obsolete; the ore hearth in recent years has become of considerable importance with a limited class of ores; the blast furnace remains the leading method, since it can treat economically all kinds of ores.

Development of Smelting Processes.—The most primitive form of lead smelting in the United States was practiced with the log and ash furnaces in Missouri prior to 1850. They employed the roast-reaction system of smelting and were applicable only to nonargentiferous galenas of very high grade in lead. They were for the most part displaced about 1840 by the Scotch-hearth furnace. Later, reverberatory furnaces of the Flintshire type went into use, but never extensively nor with such success as to develop a permanent metallurgical practice. The Scotch hearth, however, has survived, and in its modern development is the basis of a high and efficient process in the treatment of certain classes of ore, especially high-grade nonargentiferous galenas.

Neither the Scotch-hearth nor the reverberatory furnace is well adapted to the treatment of argentiferous ore, or to the treatment of ore containing less than 60 per cent lead, while the smelting of carbonate ores alone by either method is not feasible. Neither gives a finished slag or waste product at one operation that can be discarded, and final treatment of their product is usually completed in the blast furnace. For these reasons, by far the major part of the world's lead is produced by smelting in the blast furnace.

In smelting any type of lead ore by any method, the sulphur must be largely removed and the impurities must be combined in a slag, fusible at approximately 1100 to 1200°C., and of specific gravity not to exceed 3.6. In blast-furnace smelting, the slag must be of a composition that will form at the right point in the smelting process, will be thoroughly liquid, in order to ensure a satisfactory separation from the matte, and will require the minimum consumption of fuel, the chief part of which in blast-furnace smelting is always consumed in effecting the formation of the slag.

The sulphur is eliminated in various ways, which may be enumerated as follows:

1. **Roasting.**—Lead ores are usually low in sulphur and therefore are not self-burning in the ordinary roasting furnace. As the decomposition of lead sulphate is effected only by reaction with silica, forming lead silicates, the necessary temperature must be supplied chiefly by the combustion of carbonaceous fuel. The roasting of lead ore may be done in three ways.

a. Ordinary roasting in which the ore is simply desulphurized, at the same time being more or less sintered. Often the ore is partially fused, so that upon withdrawing from the furnace it crusts or may be pounded into cakes.

b. Slag roasting, in which the ore is completely fused.

c. Sintering, in which the sulphides are self-burned and sintered under air blast, either pressure or suction.

The object of roasting is to reduce the sulphur to as low a point as possible, without entailing undue losses in other directions. The sulphur is more completely eliminated by sintering than by ordinary roasting, and more completely by slag roasting than by sintering. At the same time, the loss of lead by volatilization is heavily increased, and in slag roasting it is so high that the process has been abandoned in the United States, save in one or two instances. Ordinary roasting, by which the sulphur is reduced to about 4 per cent, is supplemented by sintering to reduce the sulphur still further and to produce a blast-furnace material of desirable character.

The subject of roasting in general finds detailed treatment in a section of the first volume, "Principles and Processes."

2. *Roast-Reaction.*—Lead sulphide burned partially to sulphate reacts with undecomposed sulphide, setting free metallic lead and sulphur dioxide. This process is effected in the reverberatory smelting furnace, where the charge is first partially roasted and the reaction is then effected under increase of temperature, also in the Scotch hearth wherein the roasting and reacting go on simultaneously. In the modern blast furnace, which is operated under conditions promoting oxidation, roasting and reacting play an important part.

3. *Precipitation.*—Ore is charged raw into the blast furnace, and the lead sulphide is decomposed by iron, precipitating metallic lead, while the sulphur combines with the iron, forming a matte, from which the sulphur is subsequently eliminated by roasting. The quantity of matte to be roasted is apt to be as much as the quantity of ore smelted, but the loss of lead is less than if the ore were roasted originally. There are other drawbacks, however, and this method, which has never had any wide application in the United States, is now employed by itself in only one or two instances. The reaction takes place to some extent in any blast furnace, however, and it, together with the reaction between the sulphide and sulphate described under the previous heading, is largely relied on in modern practice in the blast furnace. Galena of high grade is sometimes charged raw into the blast furnace to save the comparatively high loss of lead which is suffered in ordinary roasting. Precipitation smelting may also be done in the reverberatory furnace, but this method is inefficient and has seldom been practiced either in America or Europe.

After elimination of sulphur by ordinary roasting or by sintering, the ore is ready for smelting in the blast furnace. Naturally oxidized ores may go of course to the blast furnace without any preliminary treatment, save breaking to the proper size.

The universal application of flotation concentration and the high grade and extreme fineness of the concentrate produced have caused sintering to be adopted as a necessary step in blast-furnace smelting. This, in turn, has led to the incorporation of practically all constituents of the blast-furnace charge, including limestone, in the sinter, producing a uniform, self-fluxing charge material, whose characteristics and composition are under close control. The blast-furnace charge commonly consists of 75 to 90 per cent sinter containing 40 to 55 per cent lead, producing a lead content of about 40 per cent in the total charge exclusive of coke.

The Function of the Blast Furnace.—The function of the blast furnace is to reduce the metal and to slag the impurities so that a separation can be made. This separation is effected by the difference in specific gravity of the various products. The specific gravity of liquid (molten) lead is about 10.5, that of matte ordinarily ranges from 4.5 to 5. In order to ensure a satisfactory separation of matte and slag, the specific gravity of the latter should be at least 1.0 lower than the lightest matte. Both the matte and the slag must be thoroughly liquid at the temperature of issue from the furnace. Consequently, the matte must be free from components that make it mushy, such as zinc sulphide, and the slag must be of a composition that is easily fusible at 1100 to 1200°C. The cleanness of the slag, *i.e.*, its freedom from gold, silver, lead, and copper, is dependent chiefly on these physical conditions. The lead content of a good slag should not exceed 1 per cent; the silver content should not exceed 0.2 oz.; the gold content should not be more than a trace. In order to achieve such a result, the specific gravity of the slag should not be more than 3.6, and it should be of approved chemical composition.

In making a slag, the metallurgist is practically limited by the elements that commonly occur in ores, and to cheap fluxes like limestone. The commercial slag is a silicate of two or more bases. The fundamental constituents are silica, iron, and

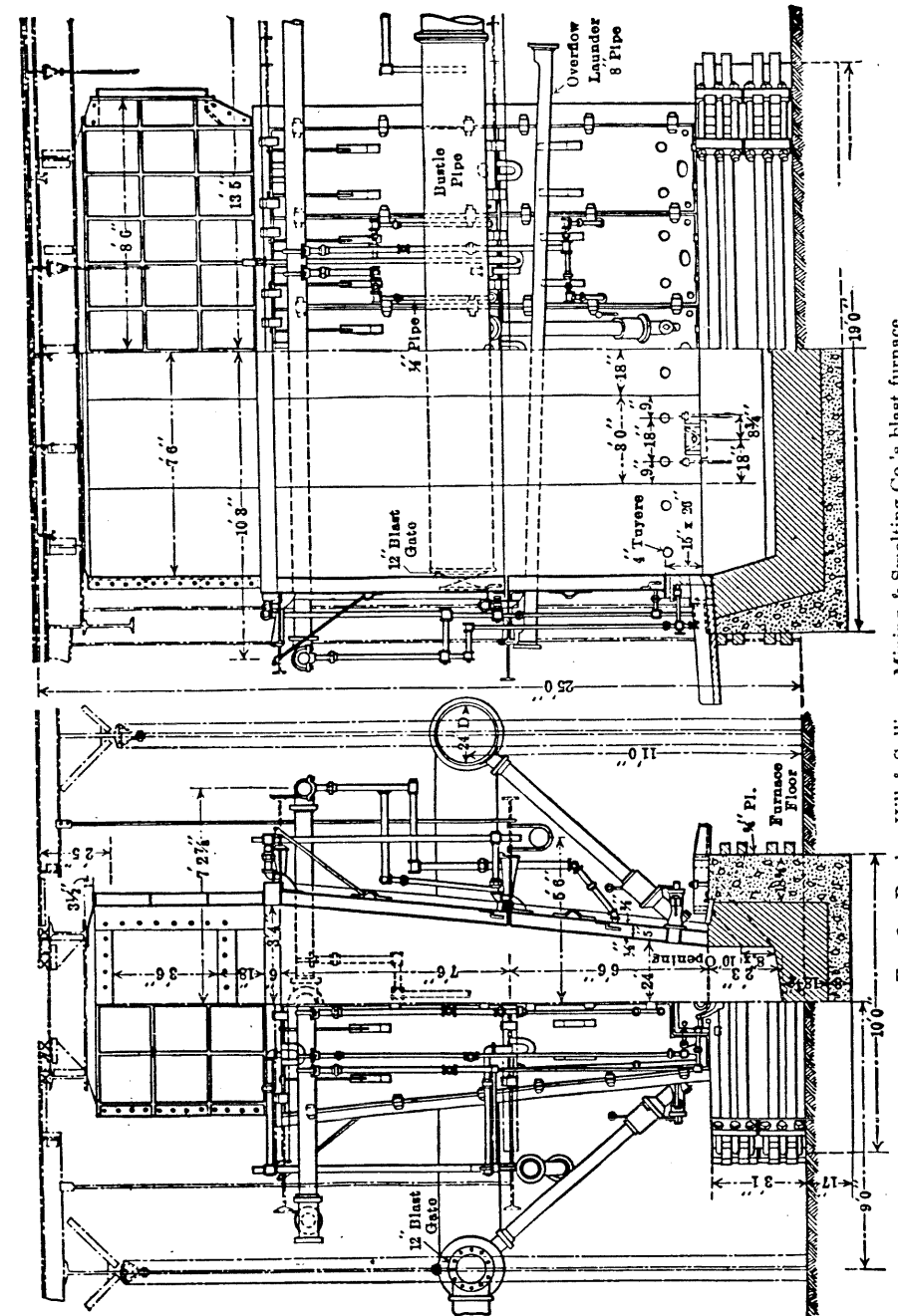


FIG. 2.—Bunker Hill & Sullivan Mining & Smelting Co.'s Blast furnace.

lime. The iron may be replaced to some extent by manganese, and the lime to some extent by magnesia, zinc oxide, and barium oxide. These elements ordinarily constitute 90 per cent of the slag. The remainder is chiefly alumina, barium sulphate, and sodium and potassium oxides. In preparing the furnace charge, a mixture of ores and fluxes is made in such proportions as to produce a slag of the desired composition. In lead smelting the permissible range in silica content is rather narrow, varying from 20 to 36 per cent, and ordinarily also the percentages of ferrous oxide and lime range only within narrow limits; the percentages stated nominally as ferrous oxide and lime include their equivalent, respectively, of manganese oxide and magnesia.

The efficiency of the lead-smelting process depends chiefly on (1) the method of sulphur elimination, affecting the cost of the operation, the loss of gold, silver, and lead, and the physical condition of the product delivered to the blast furnace; (2) the design and construction of the blast furnace and its accessories, the method of operation, the physical condition of the material charged, the correct composition of the slag, the character of the bullion produced, and the means of collecting dust and fume; (3) the means for handling products throughout the process.

The better the character of the slag, the faster will be the running of the furnace, *i.e.*, the greater the quantity of charge smelted per square foot of hearth area¹ and the lower the loss of lead and silver in the slag and in the fume. The lower the proportion of very fine material in the charge, the faster will be the running of the furnace and the smaller the percentage of flue dust to be collected and rehandled. The better the character of the bullion, the less irregularity in the operation of the furnace and the less the cost of refining. A detailed consideration of all these governing and largely interdependent factors is possible only in a much larger volume than here presented and will be found in the standard treatises on the subject. It is aimed here to emphasize the general principles of the art and the predominant effect of the make-up of the furnace charge in determining the cost and efficiency of the smelting process. It may be said that the successful development of the silver-lead smelting industry hinges on this matter. As the histories of the various lead-smelting districts are examined, it will appear strikingly how the process was quickly made successful in those which had the advantage of a self-fluxing ore, how it was struggled with in many other districts, and how, as lead smelting became a well understood art, it came to be recognized that an assured and adequate supply of the right classes of ore was the fundamental for the inauguration of a successful business.

Given supplies of silica, iron, and lime, there is no difficulty in producing a slag of any desired composition, but the smelting might be so costly as to be unprofitable. The cost of smelting is properly based on the charge, *i.e.*, all the material except the fuel that is put through the furnace. It is the aim of the metallurgist to have the ore in the charge at the maximum possible percentage, *i.e.*, it is sought to obtain all the necessary fluxing elements in a proper proportion in the ores purchased for smelting, since the time, fuel, and labor required to smelt a pound of flux are the same as for a pound of ore, and for each pound of flux put into the charge there is one pound less of ore. It is, consequently, of the utmost importance to the smelter to be able to secure ores that, upon mixture, will contain the proper proportion of slag-forming substances and will obviate the necessity of making up the proper proportion by the addition of barren fluxes. It is seldom possible to attain the acme of that condition, a small proportion of limestone usually must be added to the charge, and there is always a certain quantity of foul slag, flue dust, roasted matte, and other products that must be resmelted. In the modern American practice of silver-lead smelting, the ore in the charge amounts usually to 80 per cent or more.²

¹ The hearth area is the horizontal section of the furnace on the line of the tuyères.

² This means 80 per cent or more of the charge, exclusive of the return slag which is used in larger or smaller quantities, often rather large, to facilitate the running of the furnace.

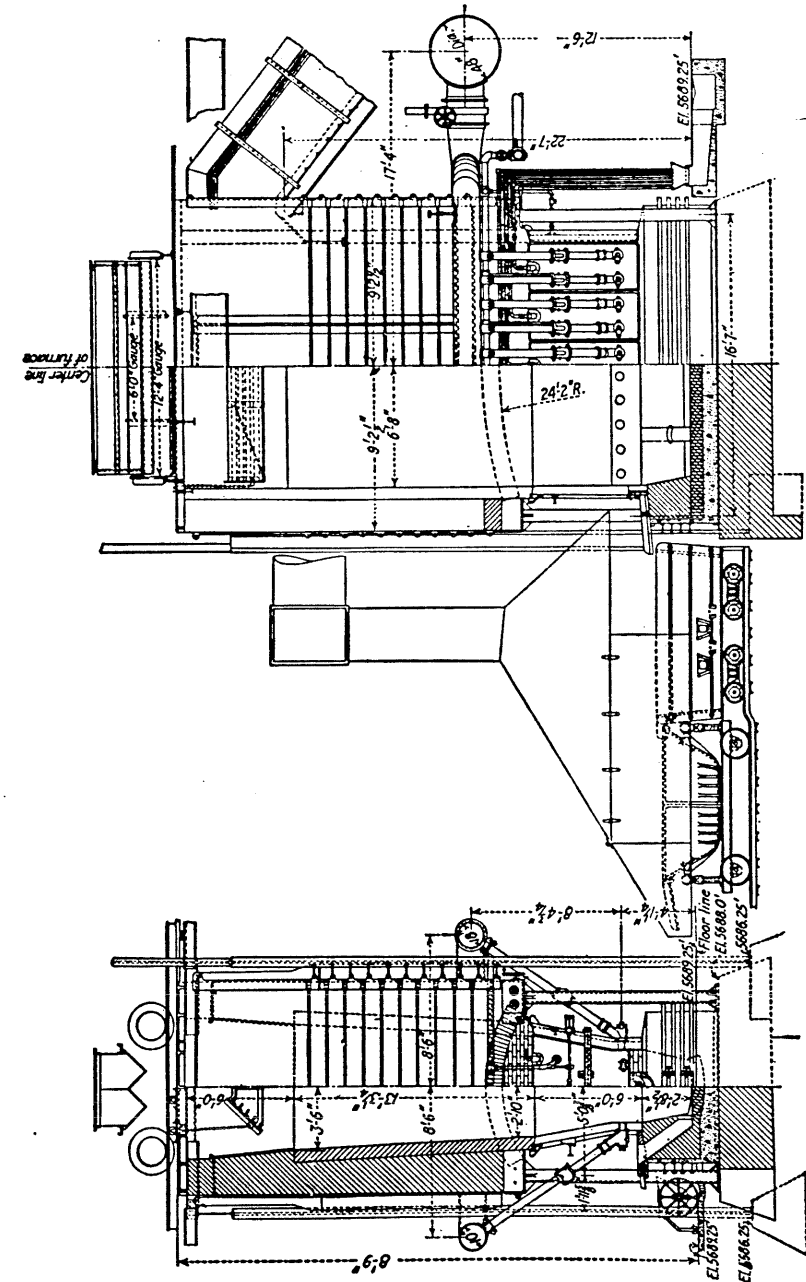


Fig. 3.—Lead blast furnace used at Midvale after 1019.

The practice of the metallurgy of lead has resolved itself at the present time into smelting in the blast furnace for silver-bearing ores and smelting in the Scotch hearth for silver-free ores. In both kinds of smelting the smoke and fume are filtered in baghouses using woolen or asbestos bags. Electrostatic precipitation is well adapted for the collection of fume from all lead-smelting operations and is cheaper in first cost than large baghouse installations. It has been universally adopted for lead-roaster and sinter-plant fume collection, since these gases usually carry elemental sulphur which frequently causes disastrous fires and explosions in baghouses.

With proper fume collection, smelting in the blast furnace yields an over-all recovery in bullion of 95 to 98 per cent of the lead charged. Recoveries of 98 per cent lead are obtained in smelting high-grade galena ores in the Scotch hearth. The two methods of smelting are applied under radically different conditions. In silver-lead smelting in the blast furnace, the prime function of the lead is to act as a collector for the precious metals. The percentage of lead in the blast furnace charge in different smelteries ranges from 10 per cent in blast-smelting crude ores to as high as 50 per cent where the charge is practically all sinter produced from high-grade concentrate. In any case the proportion of slag to ore that is made is much higher than in the treatment of high-grade galena ore in the Scotch hearth, and consequently loss of metal in the slag is higher in the blast furnace. The Scotch-hearth method of smelting has been confined to the treatment of nonargentiferous galena containing 60 per cent of lead or upward. This method of smelting has been improved by the introduction of the Newnam mechanical rabbler, which has reduced labor and improved working conditions, an important item in view of the severity of the latter, especially in hot weather.

The Blast Furnace.—The lead blast furnace has become in recent years practically standardized at modern plants. Materials going into and products coming out of the furnace are handled in almost as many different ways as there are plants in the industry, but in this respect also there is a tendency toward standardization, as hand labor becomes gradually replaced by mechanical equipment. Lead blast furnaces have certain common features, in general the following: rectangular-horizontal section, tapering sides with boshes, straight end, a water-jacketed smelting zone, internal crucible, and the Arents siphon tap for bullion. The circular water-jacketed furnace is used only to smelt at intervals small quantities of intermediary products of a refinery, or for ore smelting in remote localities. The brick shaft common with most ore furnaces has in some plants been replaced in its lower portion by steel water jackets. Furnaces having an entire shaft made up of water jackets are successful, but there is some question of the necessity of the top tier of jackets, and the fuel consumption is said to be higher on such furnaces.

With the increase in size of furnaces and of smelting plants, the transportation of ore flux and fuel by teams and wheelbarrows in the early plants became impossible and reliance on hand labor for manipulation less and less efficient. These early methods have given way to mechanical traction and handling. The necessary apparatus for removing slag from the early small-size furnaces treating mainly oxide ores consisted simply of pots pushed by laborers. As oxide ores were replaced by sulphide, matte handling became a problem in connection with slag handling, solved by extra settling pots which have now given way to large forehearth. As tonnages continued to increase and speiss, dross, furnace accretions, and refractory slags came into the picture in the various smelting centers, compressed air, water, steam, and electric power were brought into play, and mechanical traction, slag granulation, and mechanical furnace manipulation in general are found throughout the industry.

The waste gases in early lead smelting escaped to the atmosphere, carrying damage to crops and man in the immediate vicinity of the plant and resulting in a very con-

siderable loss of metal values. In later periods, settling chambers for catching dust from the smoke stream were provided; these have been supplemented and replaced by baghouses for filtering and by electrostatic apparatus for precipitating the dust and fume. The primitive blowing engines, adequate for blast requirements at first, have been superseded by rotary positive pressure blowers and centrifugal compressors.

General Features of Blast-furnace Design.—The weight of a modern furnace with brick shaft is something over 100 tons. The shaft, the heaviest part, is carried on four cast-iron or steel columns, one at each corner, resting on a concrete foundation extending about 3 ft. beyond the bedplate and supporting columns.

A comparative tabulation of data of design and operation of blast furnaces, based upon a tabulation originally prepared by Hofman,¹ is given in Table 4.

The horizontal section of the furnace is rectangular, the width is most commonly 48 in., ranging from 36 to 63 in. The distance between tuyères is limited owing to the excessive blast pressure that would be required to penetrate to the center of a larger furnace and that would cause excessive volatilization of lead. When furnace charges consisted largely of fine material, the usual distance was 42 in., and this is still a common diameter of small furnaces. With sintered ore and a coarser charge, this dimension increased to 54 and to 63 in., although 44 and 48 in. are the more common figures.

Enlargement of the lead blast furnace has taken the direction, inevitably, of increased lengths rather than width, doubling from the original 60 to 120-in. and later increasing to 160, 192, and 270 in. The limit to which the length of a lead blast furnace can be efficiently increased is an open question. A normal crew can serve a furnace, say, 192 in. long; if this length is increased, additional men are necessary, and the additional tonnage obtained may not be equivalent to the added cost of labor. No great success was at first attained in imitating, on the lead furnace, the great increase in length that brought about such a notable development of the copper blast furnace. Some experiments with furnaces of this type were made as early as 1915 in which the furnace design amounted to practically two normal lead blast furnaces placed back to back with double complements of slag tap and lead well. The balance in a lead blast furnace operating on crude ore is a more delicate one than in a copper furnace, which probably accounted for the failure of many such furnaces to operate successfully. When a lead blast furnace becomes unsatisfactory in operation, it is usually cheaper to blow down the furnace, bar out, and start fresh instead of attempting to nurse it back to normal work. With a copper furnace this is done more readily, and with less loss of metal.

The operation of the lead blast furnace on crude ore and with a small proportion of sinter is delicate owing to the large number of variables that are beyond the control of the furnace operator. However, the increase in percentage of sinter on the charge has resulted in greater uniformity in the condition of the charge in all respects, and the operation has become much more stable.

At Trail, B.C., experiments with increased width and length and smaller tuyère diameter led to the development of a blast-furnace design shown in Fig. 4. This furnace is 270 in. long and 63 in. wide at the tuyères. The bosh increases the width to 84 in. at 5 ft. 8 in. above the tuyères. The furnace has 36 2½-in. tuyères on each side, and these have been shown to give a much better distribution of air than the smaller number of larger tuyères.

This furnace has been very successful in operation and has developed a much higher smelting rate than narrow furnaces of the same length.

The vertical section of a lead blast furnace is marked by an inward "bosh" of the side wall and a contracted tuyère section. This contraction secures a more rapid

¹ HOFMAN, "Metallurgy of Lead," McGraw-Hill Book Company, Inc., 1918.

TABLE 4.—BLAST FURNACES

	National Lead Co., Collinsville, Ill.†	Consol. M. & S. Co., Trail, B. C.	U. S. S. R. & M. Co., Midvale, Utah	Selby, Calif.	Arkansas Valley, Colo.	Murray, Utah
Horizontal section at throat (feed floor), inches.....	156 X 54	84 X 180	95 X 160	60 X 156	84 X 180	93 X 176
Area at throat, square feet.....	58.5	105	105.55	65	105	113.60
Horizontal section at tuyères, inches.....	36 X 126	50 X 180	48 X 160	36 X 144	44 X 102	48 X 176
Area at tuyères, square feet.....	31	126.9	33.33	36	49.5	58.60
Ratio throat to hearth area.....	1.85	17 ft. 9 in.	1.98	1.80	2.12	1.94
Height, tuyères to hearth area.....	20 ft. 9 in.	15 ft. 3 in.	24 ft. 8 in.	27 ft. 4 in.	19 ft. 6 in.	24 ft. 6 in.
Height, active or working.....	13 ft. 9 in.	15 ft. 3 in.	16 ft. 0 in.	21 ft. 6 in.	19 ft. 6 in.	10 ft.
Height, tuyères to top of crucible, inches.....	11	Steel	13	12	16	15
Water jackets, cast iron or steel.....	48 2E	68 2E	78 1E	Cast iron	Steel	Steel
Water jackets, number on one side and end.....	4	14	14	88 3E	48 1E	68 2E
Boeh, height.....	3 ft. 2 in.	4 ft. 10 in.	6 ft. 0 in.	4 ft. 0 in.	5 ft. 0 in.	5 ft. 11 in.
Boeh, inches per foot, height.....	3.5	2.95	4.41	3 ft. 1 1/2 in.	3 ft. 2 in.	4 ft. 2 3/4 in.
Tuyères, number on a side.....	8	12	10	3.87	2.21	2.365
Tuyères, diameter, inches.....	4	4	4	8	12	10
Tuyère ratio.....	6.4	4	4.71	3 1/4	4	4 1/4
Crucible, section at top, inches.....	116 X 36	180 X 50	100 X 48	144 X 36	102 X 44	100 X 44
Crucible, section at bottom, inches.....	116 X 36	168 X 50	151 X 30	144 X 36	148 X 24	100 X 44
Crucible, depth, inches.....	27	24	32.5	40.000	15 and 27.5	30
Crucible, holds pounds lead.....	28,000	85,000	60 in. from front	40,000	40,000	80,000
Lead well, position.....	Near rear end	8 X 10 in.	6 X 6 in.	Center	31 in. from front	40 in. from front
Lead well, area of basin, inches.....	8.5 X 8.5 in.	12 X 14	12 X 12	6 X 8 in.	12 1/4 X 13 1/2 in.	9 X 14 in.
Lead well, height of top of basin above top crucible, inches.....	10 X 10	6	10	9 X 9	8 X 13 1/2	9 X 9
Forehearth, inside length X width X depth, inches.....	63 X 30 X 30	60 diam. 30 deep, circular	108 X 54 X 12	72 X 96 X 27 1/2	82 X 41 X 38	97 1/2 X 43 1/2 X 34
Forehearth, capacity, cubic feet.....	32.8	30	40	68	73	83.5
Waste slag pots, capacity each, cubic feet.....	21	(Granulate)	28	95	23	25
Charge (ore and flux), weight, pounds.....	8000	6000	8000	10,000	6000	8000
Charge, sinter, per cent.....	30	80	30-65	76	35	52.4
Charge in 24 hr., short tons.....	248	350	160-300	200	160	263
Charge, tons per square foot hearth area, 24 hr.....	7.9*	5.6	4.52	5.55	3.12	4.48
Pb, per cent of charge.....	39.8	Small	11-18	20-30	11	12.8
Cu, per cent of charge.....	1.0	1.0	0.7-1.0	1.0	0.8	1.02
S, per cent of charge.....	3.0	1.0	2.5-3.8	3.0	4.0	3.5

TABLE 4.—BLAST FURNACES.—(Continued)

	National Lead Co., Collinsville, Ill.†	Consol. M. & S. Co., Trail, B. C.	U. S. S. R. & M. Co., Midvale, Utah	Selby, Calif.	Arkansas Valley, Colo.	Murray, Utah
Coke, per cent of charge.....	10.0	11.5	12.0	12.5	12.0	11.85
Coke, per cent of carbon.....	82.0	82.5	85.0	82	76.0	81.4
Coke, cubic feet per minute.....	8000	13.0	11.0	13.0	21.5	14.1
Blast, ounce pressure.....	20-32	48	5300	6000	5000-6000
Cooling water, for jackets, gallons per hour.....	9000	36-42	40	Variable
Men in 8 hr. shift, regular crew.....	7	6	Variable	Variable	35
Lead bullion, at times Ag, Au, per ton.....	10.0	50.0	80-100	245	109.3.00	104.0.41
Spence, per cent charge.....	None	Small	0.5
Matts, lb, per cent.....	8.3	None	10.0	10.0	9	7.8
Matts, Cu, per cent.....	7.0	10-18	9-10	12	13.7
Matts, Ag, ounces per ton.....	5.2	6-12	4-8	12	11.7
Slag, SiO ₂ , per cent.....	29.1	18.0	30-50	20-40	55	44.3
Slag, FeO, per cent.....	33.7	42.0	38.0	40-50	28-32	30-34
Slag, Co(Mn)O, per cent.....	16.5	10.5	22.0	17-19	37-31	38-31
Slag, Al ₂ O ₃ , per cent.....	4.0	5.5	3.0	3.5	5.0	18-21
Slag, ZnO, per cent.....	11.4	19.0	5-9	6.0	7.5	3.0
Slag, Pb, per cent.....	1.5	1.5	0.6-1.2	0.9	1.0	9.0
Slag, Ag, ounces per ton.....	0.2	0.15	0.5-0.7	1.0	0.5	0.81
Slag, Cu, per cent.....	0.51
Slag, specific gravity.....	3.14

* Tuyère-ratio = square inch tuyère area: square feet hearth area.
† Charge almost exclusively gray slag from ore hearths.
‡ Smelting discontinued, 1935.

TABLE 4.—BLAST FURNACES.—(Continued)

	American Smelting & Refining Co.				St. Joseph Lead Co., Herculesum, Mo.	Sulphide Corporation, Phoenix, N. S. W.	Bunker Hill & Sullivan M. & C. Co., Kellogg, Idaho	Cong. Mining & Smelting Co., Trail, B. C.
	Esst Helena, Mont.		Federal, Ill.					
	Fees 1, 2, 3	Fee 4	Fees 1, 2, 3	Fee 4				
Horizontal section at throat (feed floor), inches.....	84 X 192	90 X 170	78 X 144		84 X 192	123 X 201	80 X 180	84 X 270
Area at throat, square feet.....	112	106	78		112	171.07	100	157.50
Horizontal section at tuyères, inches.....	42 X 192	48 X 136	42 X 144		50 X 192	60 X 138	48 X 180	63 X 270
Area at tuyères, square feet.....	56	45	42		67	57.6	60	118.0
Ratio throat to hearth area.....	2	2.4	1.86		1.66	2.98	1.06	1.33
Height, tuyères to throat (feed floor), inches.....	24 ft. 1 in.	24 ft. 1 in.	21 ft. 0 in.		20 ft. 0 in.	29 ft. 8 in.	20 ft. 9 in.	16.3 in.
Height, active or working, inches.....	15 ft. 6 in.	Thimble	14 ft. 6 in.		11 ft. 0 in.	24-28 ft.	14 ft. 10 in.	15.3 in.
Height, tuyères to top of crucible, inches.....	10	12			12	16	14	21.5
Water jackets, cast-iron or steel.....	Steel	Cast iron	Steel		Steel	Cast iron	Steel	Steel
Water jackets, number on one side and end.....	128 4E	58 2E	58 1E		48 1E	88 3E	58 4E	98 2E
Water jackets, height.....	14 ft. (6 ft. 6 in. + 7 ft. 6 in.)	4 ft. 6 in.	5 ft. 9 in.		6 ft. 0 in.	6 ft. 6 in.	14 ft. (6 ft. 6 in. + 7 ft. 6 in.)	14 ft. 9 3/4 in.
Booth height.....	4 ft. 0 in.	3 ft. 0 in.	4 ft. 8 in.		3 ft. 11 in.	4 ft. 4 in.	14 ft. 0 in.	5 ft. 8 in.
Tuyères, inches per foot, height.....	0.75	0.64	2		3	4.2	1.23	3.7
Tuyères, number on a side.....	12	8	8		12	7	10	36
Tuyères, diameter, inches.....	4 1/4	5	4		4.37	3	4	2.6
Tuyères, ratio.....	3.50	4.40	4.70		5.37	1.72	4.19	2.9
Crucible, section at top, inches.....	192 X 42	136 X 48	42 X 144		48 X 188	54 X 132	45 X 180	63 X 270
Crucible, depth, inches.....	192 X 42	120 X 48	24 X 144		48 X 108	54 X 132	45 X 108	See Fig. 4
Crucible, holds pounds lead.....	36	33	24		29	20	20	See Fig. 4
Lead well, position.....	90,000	80,000	40,000		1t 5th tuyère	38,500	80,000	68,000
Lead well, area of channel, inches.....	At second jacket	At second jacket	48 in. from front		8 X 8 in.	Concrete	54 in. from front	45 in. from front
Lead well, height of top of basin, inches.....	24 sq. in.	24 sq. in.	4 X 4 in.		10 X 16 in.	4 X 4 in.	8 X 10 in.	
Lead well, height of top of basin above top crucible, inches.....	9	9	4		6	10	10	

	102 X 42 X 33		102 X 42 X 33		98 X 51 X 35		Reverb. furnace 10 ft. 6 in. X 18 ft.	
	Forehearth, inside length X width X depth, inches.		Forehearth, inside length X width X depth, inches.		Forehearth, inside length X width X depth, inches.		Reverb. furnace 10 ft. 6 in. X 18 ft.	
	83	28	83	28	100	23	Two circular: 6 ft. 2 in. top 3 ft. 8 in. bottom	40 tons
Forehearth, capacity, cubic feet.....	9000	9000	9000	9000	12,000	75-85	3,000	3250
Waste slag Pots, capacity each, cubic feet.....	260	260	220	220	374	336	87	80
Charge (ore and flux), weight, pounds.....	4.7	24-28	4.8	24-28	6.30	45-50	7.0	40
Charge, sinter, per cent.....	12.4	12.4	12.4	12.4	0.4	2.0	45	
Charge in 24 hr., short tons.....	3.0	3.0	3.0	3.0	3.0	2.0	2.0	9-11
Charge, tons per square foot hearth area, 24 hr.....	Very small	Very small	Very small	Very small	8.4	8.0	0.8-1.4	82
Pb, per cent of charge.....	12.4	12.4	12.4	12.4	82.0	12.0	78-82	15
S, per cent of charge.....	15.0	15.0	15.0	15.0	7.0	12.0	12-16	
Coke, per cent of charge.....	7000	7000	5000	5000	7000	7500	6000-7000	
Coke, per cent of ash.....	32-36	32-36	32-36	32-36	22-30	70	20-82	
Blast, cubic feet per minute.....	6000	6000	5100	5100	15,000	12,000		
Blast, ounces pressure.....	3	3	3	3				
Cooling water for jackets, gallons per hour.....	80	80	80	80	Ag 3.8-Au 0	80	Ag 80-100 Au 0-25	45.0
Men in 8-hr. shift, regular crew.....	None	None	None	None	None	None	None	
Lead bullion, ounces Ag, Au, per ton.....	None	None	None	None	Ag 3.8-Au 0	None	None	
Spells, per cent charge.....	None	None	None	None	None	None	None	
Matte, per cent charge.....	None	None	None	None	2.5	None	None	
Matte, Pb, per cent.....	None	None	None	None	15.1	None	None	
Matte, Cu, per cent.....	None	None	None	None	11.1	None	None	
Matte, Ag, ounces per ton.....	None	None	None	None	0.75	None	None	
Slag, SiO ₂ , per cent.....	21-25	21-25	21-25	21-25	26.8	38	22.0	19.0
Slag, Fe(Mn)O, per cent.....	45-49	45-49	45-49	45-49	36.8	17	35-28	31.1
Slag, Ca(Mg)O, per cent.....	13-15	13-15	13-15	13-15	14-16	5	16-21	9.0
Slag, Al ₂ O ₃ , per cent.....	3.6	3.6	3.6	3.6	7.5	12	3.8	5.0
Slag, ZnO, per cent.....	15.0	15.0	15.0	15.0	12.0	12	16.5	23.1
Slag, Pb, per cent.....	1.0	1.0	1.0	1.0	6.5	0.0	1.2	3.5
Slag, Ag, ounces per ton.....	0.35	0.35	0.30	0.30	1.0	0.0	0.15-0.40	0.10
Slag, Cu, per cent.....					Trace		0.12	0.15
Slag, specific gravity.....			3.65				3.4	

1 Tuyère ratio = square inch tuyère area: square feet hearth area.
 2 Charge almost exclusive of gray slag from ore hearths.
 3 Smelting discontinued, 1933.

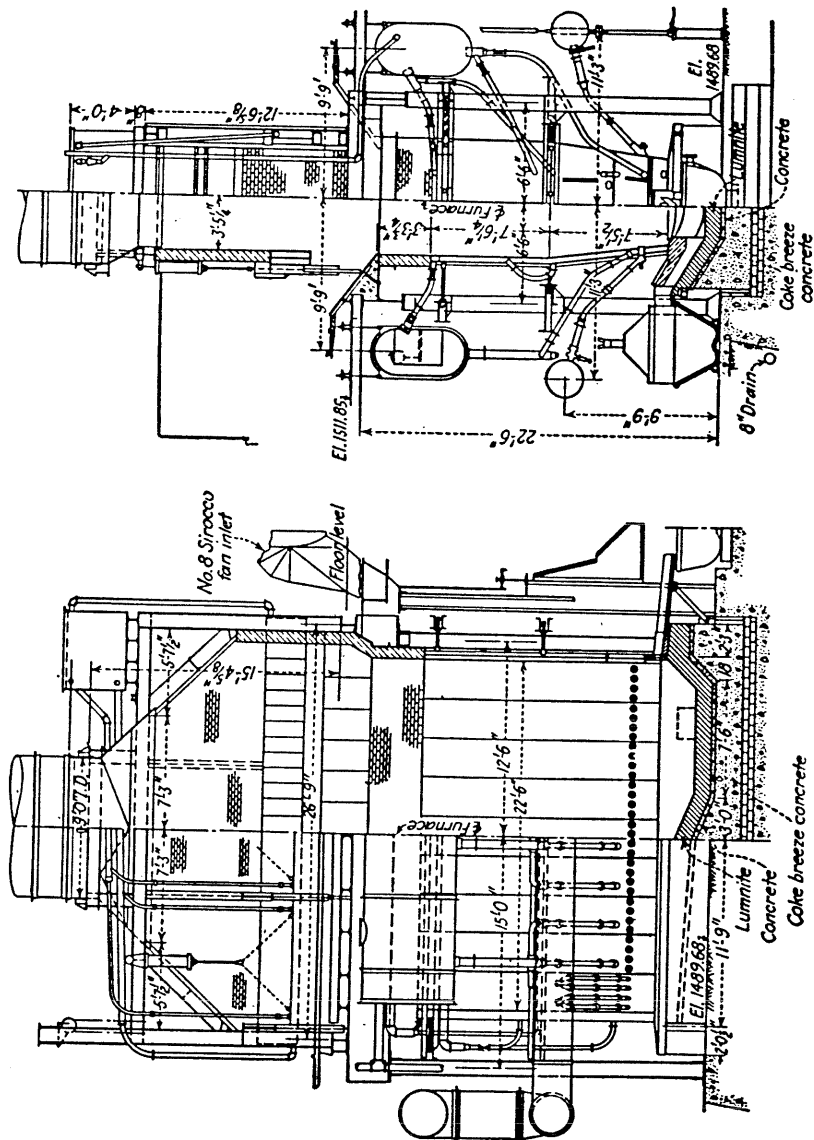


Fig. 4.—Number 10 lead blast furnace at Trail, B. C.

combustion and concentrated intensified heat, resulting in a quicker fusion and more complete decomposition of lead sulphide. When, higher up in the shaft, the width is suddenly increased by the boshes, the gases formed at the tuyères are checked in their upward velocity and more evenly diffused through the descending ore column, giving up their heat to the charge and preparing it for subsequent fusion. In addition the spread of the gases decreases the amount of flue dust carried out of the furnace.

The ends of the furnace are usually without bosh, although some of the earlier plants have end bosh as well as side. Experience generally indicates that the end bosh tends to bring about wall accretions.

Extending upward from the rim of the crucible to the bottom of the brick shaft are the water jackets. These are double-walled steel sections through which water is circulated. They enclose the smelting zone and prevent corrosion of this portion of the shaft by slag. The height to which the shaft is water-jacketed varies in furnace design; however, complete water-jacketing of the entire shaft is generally considered undesirable or unnecessary.

A substantial heat loss, as high at 10 per cent, occurs in the jacket waters. This is reduced and a more uniform operation secured by a closed, or thermosyphon, system for circulation of the cooling water.

The tuyères are circular orifices through the jackets, $2\frac{1}{2}$ to $4\frac{1}{2}$ in. in diameter, usually placed about 13 in. above the rim of the crucible. Through them the blast of air is introduced into the smelting zone. They are placed along the sides and sometimes in the back of the furnace. The side tuyères are spaced 6 to 20 in. apart. The modern furnace takes 5000 to 8000 cu. ft. of air per minute.

The hearth, or crucible, enclosed in brick, concrete, and ironwork, extends from the foundation to the bottom of the jackets. The lines of the crucible are usually a continuation of those of the shaft, and the depth of the crucible ranges from 20 to 36 in., commonly about 30. The crucible, except with very pure bullion, gradually becomes filled with a dross of higher melting point than the bullion, except at the point adjacent to the siphon tap where the temperature is kept higher by the constant withdrawal of bullion. As a result, in most furnaces the crucible is filled with brick or concrete to form a sloping hearth draining to a small wall or sump at the front connecting to the siphon tap.

The Arents siphon lead tap is an opening in the side wall of the crucible. It consists of an inclined square channel about 8×12 in. in cross section, leading from the bottom of the crucible side wall, inside, to the top on the outside. At its top, outside the furnace, the channel is enlarged into a bowl-shaped basin, called the lead well. This tap is placed either at the middle of one of the sides or, preferably, a little toward the front of the furnace. When the furnace is running, the crucible should remain full, or nearly full, of lead. The lead in the well will stand higher than the level inside, owing to the pressure of the blast and weight of the charge on the interior surface. The discharge of the lead well is at a level 4 to 10 in. above the top of the crucible. The furnaceman keeps the lead in the well at a height that maintains the lead in the crucible at the top of the hearth, gauging this by experience in tapping. Ordinarily, the furnaceman will close up the lead discharge periodically in order to force the lead in the crucible to rise to a level where some begins to run out with the slag, so that he may know that all speiss, matte, and zinc mush have been cleaned out of the furnace when the furnace slag is tapped "to a blow." With charges running high in lead, 30 to 45 per cent, the lead overflows continuously from the well into a suitable lead kettle at the side of the furnace; with 10 to 15 per cent lead on the charge the well is tapped at intervals.

Handling Ores and Products.—The blast furnace may be considered as the objective point on which turns the entire transportation system and flow sheet of the plant.

The receiving and disposing of raw materials, fluxes, fuel, ores, for the blast furnace and the disposal of its waste, intermediate and primary products, form part of the general arrangement of the whole smelting plant, involving also the sampling and storing of materials, roasting and preparing smelting charges, and the disposition of power, water, and other necessary factors. All this involves an engineering problem of considerable magnitude, detail mention of which is beyond the scope of the present discussion. In sections of the first volume will be found the treatment of sampling, fuel, roasting and sintering, power, fume collection, slag, and other phases of smelting procedure that are more or less common to reduction plants for all metals.

Briefly stated, the products of the lead blast furnace are disposed of as follows:

1. *Lead*.—Crude lead from the lead well is usually transferred to a drossing kettle of 30 to 250 tons capacity where it is freed from impurities held in suspension or solution. This is accomplished by drossing or "poling" (mechanical stirring of the molten lead by means of compressed air or steam) and by the addition of sulphur. The impurities that rise to the surface are slightly oxidized drosses and remain on the surface of the bath, from which they are removed by skimming with a perforated disk or spoon. The agitation exposes new surfaces continually to the air, resulting in the slow oxidizing of copper, sulphur, arsenic, antimony, zinc, and iron which collect on the surface as a dross. When sulphur is added as a drossing reagent, the copper is removed as a sulphide. The kettle of molten lead is allowed to cool to about 480°C. before the dross is removed. After the dross is removed, the lead is air-agitated until the temperature drops to about 360°C., removing constantly the accumulating dross. The temperature is then slightly raised (to about 380°C.) for the taking of "gum-drop" samples (small ladle samples weighing 0.5 assay ton each) and then to about 425°C. for casting the lead. The dross usually goes back to the blast-furnace charge, after being freed by liquation or pressing of much of its occluded lead.

Separate smelting of the dross in a reverberatory furnace for the production of matte and bullion is a recent development. This reduces the production of matte in the blast furnace and eliminates the recirculation of a considerable amount of copper and antimony.

2. *Matte and Slag*.—An imaginary cross section of the crucible of an operating furnace would show the crucible filled with lead, and floating above the lead, speiss, matte, and slag in the order given. The lead leaves the crucible through the siphon tap, which takes off at the bottom, and the other products are tapped through the tap-hole at the front of the furnace, intermittently, into an external receiver or forehearth, in which they separate in accordance with their specific gravity, speiss at the bottom, matte above speiss, and slag above matte. On top of the normal matte there is usually found a zinc mush which separates with difficulty from both slag and matte.

This zinc mush, inside the furnace, and outside as well, is the bane of lead furnace-men and metallurgists; it is the root of furnace troubles which may vary in intensity from merely unsatisfactory assays (metal losses) to the entire loss of the furnace through freezing or slagging (mushing) of tuyères. More than any other single factor, the solution of the zinc-mush difficulty is to eliminate the possibility of its formation, primarily, by the exclusion of zinc-bearing materials from the charge, or if this is impracticable, by ensuring the dead roasting of all zinc sulphide of the charge. Zinc combined with sulphur spells trouble; zinc combined with oxygen is handled and slagged with comparative ease. Zinc entering the blast-furnace slag is no longer a total loss, but in modern practice is recovered with a considerable portion of the lead by further treatment of the slag. Improvements in selective concentration and in sintering practice have been the largest factors in meeting the zinc situation. There are two other points in the lead blast-furnace manipulation of zinky charges that, although not so generally known, are recognized at certain plants as of almost equal

importance in combating zinc troubles. At Namtu, Burma, where slag zinc runs up to 30 per cent ZnO, it has become recognized that zinc troubles are not always sulphur troubles.

Some of the most troublesome work on record at the Namtu furnaces occurred when the physical condition of the sinter was quite up to the average, with sulphur only 2 per cent, furnace clean, coke good, and when the analysis of the resultant slag was in line with their best type. Trouble appeared because, although the zinc and iron were in the charge in the correct proportion, they were not there in the correct condition. No trouble is encountered when the iron necessary to satisfy the slag demands of the zinc exists in the charge in intimate association with the zinc and when, also, a comparatively small amount of slag material has to be made to carry the zinc in the concentrator; it is a really troublesome matter when the iron requisite for a heavy zinc charge has to be supplied almost entirely, as at Namtu, by the addition of limonite and, to obtain satisfactory combination, a considerable heat reaction is required. At Namtu, it is also to be noted that a slag fall of 2 to 1 is obtained by the amount of slag that has to be formed to carry the zinc, even when this slag contains 30 per cent ZnO.

At Cockle Creek, New South Wales, control of zinc troubles had been secured, prior to the shutting down of this plant of the Sulphide Corp., by smelting methods that were almost unique in lead blast-furnace practice. A combination of high ore columns (26 to 28 ft.) and high blast pressure (approximately 70 to 75 oz.) maintained an intensity of temperature at the smelting zone and a drive of the furnace that resulted in remarkable freedom from zinc accretions and trouble and gave slag carrying well under 1 per cent lead, with no unusual losses in any direction.

Where matte is made in appreciable quantities, large movable forehearth (about 8 × 4 × 4 ft.) receive the stream of slag and matte tapped from the furnace. The matte and speiss produced are trapped and accumulate in the forehearth, while the slag overflows from the top. At intervals, the matte and speiss are tapped through the side of the forehearth. The waste slag pots are removed by a locomotive and the slag disposed of either by pouring over the dump or into a granulating apparatus. In most large smelteries, this molten slag is now transferred to a slag-blowing furnace where the zinc and lead are largely removed as a fume and collected.

Formerly, all shells and crusts from waste slag pots were brought back to the blast furnace for resmelting, because of enrichment of lead and silver in the shell, fluxing requirements, and beneficial effect on the blast-furnace charge, but the practice of recent years tends to discontinue the resmelting of slag shells, substituting the resmelting of forehearth bottoms. Two forehearth in series are frequently used, with consequent throwing away of the entire contents of the slag pots. In a few instances the slag-matte mixture tapped from the blast furnace is transferred to a small reverberatory settling furnace from which matte and slag are intermittently removed. In some instances, granulating places the slag in a form that can be easily disposed of by sluicing away, when sufficient water is available; it also provides a form of slag well adapted for mixing with the sinter charge. Most large smelteries in which a considerable amount of zinc enters the blast-furnace charge now re-treat the blast-furnace slags by blowing. A large part of the zinc and lead contained in the slag is removed as oxides and is collected in the form of dust or fume in baghouses and cooling flues. A considerable tonnage of slag reclaimed from old dumps is being re-treated for recovery of its zinc and lead content by this method. The blowing furnace resembles a blast furnace in general construction. It has a rectangular water-jacketed shaft with tuyères along each side a short distance above the bottom. Molten slag is poured in at the top of the shaft to maintain a depth of molten material above the tuyère line. Pulverized coal is blown in with compressed air through the

tuyères into the bath of molten slag, the zinc and lead oxides in the slag are reduced and the metal vapors are reoxidized in a combustion chamber above the surface of the slag and are carried away through flues to the collecting equipment. The molten slag after blowing is tapped out of the furnace and disposed of.

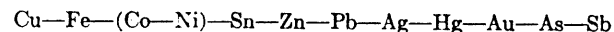
The matte contains silver, gold, lead, and copper and must all be re-treated. Three methods of re-treatment are in common use: (1) The matte is crushed or granulated, mixed with the roaster or sinter feed, and desulphurized before being returned to the blast furnace. (2) The matte is resmelted as a separate operation of "matte smelting" to lower the lead content by replacement with iron and to concentrate the copper content to a point where the matte may be sold to a copper smelter. (3) The matte is treated in a standard basic lined copper converter, with or without the addition of siliceous fluxes. Air is forced through the molten matte at a temperature of 1100° to 1200°C., oxidizing the S, Fe, and Pb. The iron is slagged as silicate by the fluxes, or as molten Fe₂O₃ if no fluxes are added. The lead is slagged or driven off with the sulphur as a basic lead-sulphate fume. The Cu, Ag, and Au remain and are combined with copper matte and reduced to metal by a continuation of the converting operation. The lead-bearing slag and lead fume produced in the converting operation are re-treated in the blast furnace.

3. *Fume and Dust.*—Hoods are placed at all points around a blast furnace where fumes arise, the pipes from all hoods lead to a main flue and exhaust fan which deliver to a baghouse or electrostatic precipitator. The gases and dust issuing from the top of the furnace, combining with the fumes from the tapping floor, travel through flues and chambers in which they drop most of their dust, and then to special condensation or filtering apparatus. The methods for recovery of flue dust and fume at lead smelteries and refineries may be classed as dry, wet, and electrostatic. In Chapter XII of the first volume the subject of dust treatment is discussed in greater detail.

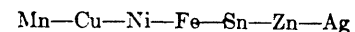
Chemistry of the Lead Blast Furnace.—The charge—ore, flux, and coke—fed at the top of the furnace is subjected as it descends through the shaft, in about 8 hr., at gradually increasing temperatures, to chemical reactions and physical changes that transform it into lead bullion, speiss, matte, slag, and gases. The two processes principally involved are reduction and precipitation, and incidentally sulphurization, at temperatures ranging from 1100 to 1200°C. at the tuyère level to 150°C. at the throat.

The principal reducing agents are C and CO. The carbon, supplied by the coke (normally 8.5 to 13 per cent of charge), acts on metallic oxides as soon as the temperature rises to a point where its affinity for oxygen is greater than that of the metal that is combined with the oxygen; this action begins at about 400°C. The products of oxidation are CO₂ and CO. The former results if the metallic oxide is easy of reduction, say below 1000°C., the latter if the oxide is difficult of reduction, perhaps above 1000°C. The reducing action of CO, which begins at about 200°C., increases with temperatures up to about 1000°C., beyond which point it falls off rapidly.

The principal agent of precipitation is iron. Other metals act as precipitants also, in conformity with their affinities for sulphur. Each metal will displace from sulphides other metals whose affinity for sulphur is weaker. According to Fournet such replacement is in the following order:



The more recent work of Schutz places the series in a slightly different order, as follows:



Precipitation, or decomposition of sulphide by metal, begins at about 900°C. and is at a maximum at tuyère level, where the furnace temperature is around 1200°C.

The precipitation reaction is reversible, however, and the complete decomposition of the metallic sulphides by iron is thus counteracted to some extent.

Descending Ore Charge.—In considering the changes in the descending ore charge, it is convenient to distinguish four zones: the zone for preparatory heating, 100 to 400°C.; the upper zone of reduction, 400 to 700°; the lower zone of reduction, 700 to 900°; and the zone of fusion, 900 to 1200°. There is no sharp line of demarcation between the zones, one passing over into the other; the reactions beginning in one zone may be finished only in the next or perhaps even the second lower down. The process of heat interception is continuous from the tuyères to the throat, or from 1200 to 100°C.

1. *Zone of Preparatory Heating (100 to 400°C.)*.—The charge fed into the furnace first gives up its hygroscopic water, then that which is chemically combined. Clayey material, limonites, and some other hydrates give up only part of this water at 400°C. The evaporation of water absorbs heat and thus assists in keeping the top of the furnace cool.

2. *Upper Zone of Reduction (400 to 700°C.)*.—The decomposition of hydrates continues, the dissociation of carbonates and of some sulphates begins. The reducing effect of CO, which theoretically begins at 200°C., becomes noticeable only at about 400°, and increases with rise of temperature up to about 900°. It will, therefore, be an active agent in reducing PbO completely to Pb, and PbSO₄ partly to PbS; it will also start the reduction of Fe₂O₃. The C of the coke, which begins to act reducingly at about 400°C. and increases as the temperature rises, will change PbO completely into Pb, and PbSO₄ partly into PbS; it will assist CO in its reduction of Fe₂O₃, and will transform CO₂ of the gas current into CO. There will further take place reactions of PbSO₄ and PbO and PbS, setting free Pb and SO₂.

3. *Lower Zone of Reduction (700 to 900°C.)*.—The reactions started in the preceding zone continue and are in part completed; the effect of C becomes more marked than that of CO. The CaSO₄ in sintered ore as well as BaSO₄ in raw ore are more or less reduced to CaS and BaS to be dissolved later on mainly by the slag. The dissociation of carbonates is about completed, CaCO₃ at 910°. The union of SiO₂ with unreduced PbO and PbSO₄ begins, as does the decomposition of PbS, PbAs₂, and PbSb₂ by Fe; sulphurization of Cu begins at about the same temperature. Matte of eutectic composition begins to soften. Everything is prepared to be liquefied and to bring to completion the chemical processes.

4. *Zone of Fusion (900 to 1200°C.)*.—The reductions of oxides, including ZnO, and decompositions of sulphides are completed; ascending Zn vapor is oxidized and sulphurized. Lead reduced in the upper parts of the furnace trickles through the charge, picking up Ag on its way, and acting possibly upon lead arsenate and antimonate; it joins the Pb set free lower down from PbS, PbAs₂, PbSb₂, and continues to take up Ag. The sulphides of eutectic composition, which softened higher up, become liquid and dissolve other sulphides to form matte with a melting point lying below that of slag formation. The slag components SiO₂, FeO, and CaO form a slag of lowest formation temperature and this, trickling downward, dissolves the remaining SiO₂, FeO, CaO, as well as other bases, such as Al₂O₃ and ZnO. Scorified PbO is set free and reduced by C to Pb. The three main products—lead, matte, and slag—settle in layers according to their specific gravities; lead passing downward through slag and matte robs them of some precious metal; matte in a similar way removes Pb, Cu, and Ag from the slag; at the contact planes of the products, interchange of components takes place to a moderate degree with a tendency to collect sulphide in matte and metal in lead. The lead passes off through the lead well; speiss, matte, and slag are tapped into the forehearth, from which slag overflows into a waste-slag pot or granulating apparatus, and speiss and matte are tapped periodically into suitable receivers.

Mechanical Feeding of Charge.—The metallurgical and practical success of a blast-furnace operation depend as much on a proper physical condition of charge and its accurate distribution in the furnace shaft, as on the actual constituents of the charge and their accurate calculation by the metallurgist in control. One of the greatest steps in the advance of lead blast-furnace work occurred when the old hand-feeding methods were replaced by mechanical feeding, about 1900, along lines developed by A. S. Dwight in Montana. This mechanical-feeding system and the general adoption of sintered products in the ore charge constitute the major improvements in the smelting of lead that have been developed in many years. Tonnages and metallurgical recoveries were enormously benefited by these steps, which almost revolutionized art.

Charge components, made up of ore, flux, fuel, and secondary products, vary greatly in size. In an ideal assortment of sizes, about one-third of the charge would

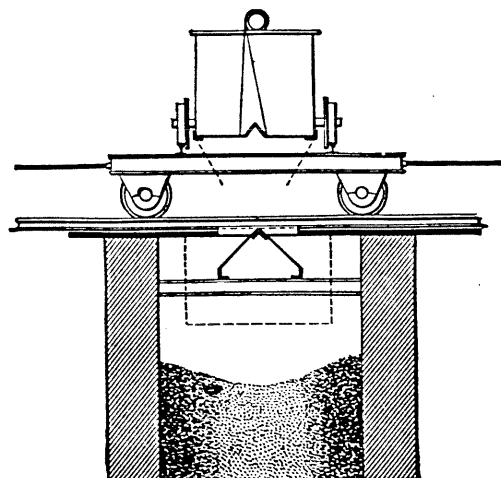


FIG. 5.—East Helena feeder with Dwight spreader.

be in pieces 5 to 2 in. in diameter, one-third 2 to $\frac{1}{2}$ in., and the remaining third $\frac{1}{2}$ in. down.

A coarse charge is preferable to a fine one, as the ascent of gases is more uniform; if too coarse, however, the gases pass up and away too quickly and do not get in their proper work on the descending charge. A fine charge obstructs the flow of gases to too great an extent, and the gases tend to break through at various points in the form of blowholes, which upset the chemistry and operation of the furnace completely and cause loss by carrying off dust and fume. In furnace work there is always the danger of fines trickling through the coarser parts of the charge and reaching the smelting zone in a crude state, chilling the furnace, and even clogging the tuyères. In modern smelting, with charges made up largely of sintered materials, the fines have been reduced to such an extent that they seldom cause trouble.

In general, the coarser parts of the charge must be placed toward the center of the shaft, and the finer material toward the side walls. The ascending gases have a tendency to hug the sides of the shaft, and their passage must be adjusted by charge distribution, so that the gas current will ascend evenly and uniformly over the whole area of the smelting column. The method of mechanical feeding developed at East Helena by Dwight in 1900 is at present in use at the majority of plants, in more or less modified forms. The principle used is shown in Fig. 5.

The contents of the charge car (4 tons) drop onto an A-shaped spreader which throws everything toward the sides of the furnace shaft where the bulk of the fines remain, while the coarser parts roll down the inclined surface or trough of the descending charge and gather along the center axis. To prevent carrying this segregation of coarse and fines too far, a modification of the Dwight spreader was adopted by W. W. Norton at Murray, Utah, in which the A-shaped spreader, instead of being a solid casting, was made up of several parts separated by open spaces, or slots, as shown in Fig. 6. The charge, on dropping onto this spreader, is not all deflected toward the side walls, but a portion falls directly through the slots and lands in the center of the furnace. A satisfactory distribution of charge results, much fine with some coarse along the sides, and much coarse with some fine along the center.

With charges in recent years made up so largely of sintered product, and the consequent greater smelting speed of the furnace, there is less danger of the heat

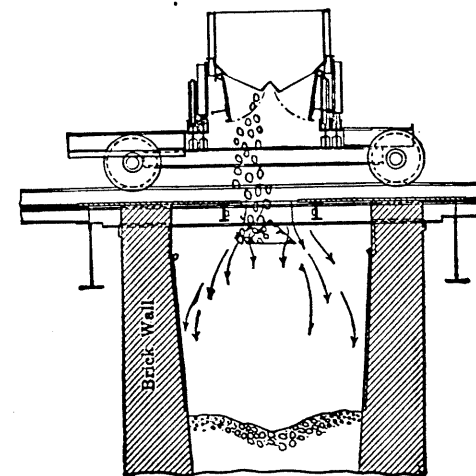


FIG. 6.—Dwight-Norton spreader.

creeping up in the furnace, and there is now a tendency to try to distribute coarse and fine more evenly through the furnace.

Smelting Lead Ores in the Reverberatory Furnace.—Until within comparatively recent years the smelting of sulphide lead ores in the reverberatory furnace was very common, especially in England, Belgium, and Austria. Since sintering has come into general use, however, reverberatory work has become nearly obsolete. In the United States in 1877 there were 56 reverberatory furnaces in operation in Missouri, in 1940 only 2.

The process involved was the roast-reaction, or air-reduction, process, based on the reactions between PbS , PbO , and $PbSO_4$ at temperatures below $1000^\circ C.$, which set free Pb and SO_2 . The precipitation process, based on the decomposition of PbS by Fe , was formerly in operation with raw lead ores in France and in the United States at one plant at Chicago, also with roasted ores in Cornwall. The precipitation process, as a separate procedure, has been given up because of high cost and heavy loss of metal.

The roast-reaction process in the reverberatory furnace involves two operations, oxidation and reduction, one following the other closely, and both being repeated several times. The finely crushed ore, spread in a layer 4 in. deep on the hearth, is heated gradually to a full red (500 to $600^\circ C.$). The roasting is carried on in such a

way that only a part of the PbS is converted into PbO and PbSO₄, the rest remaining undecomposed. The second step of the operation is that of raising the temperature to about 800°C. so that the oxygen compounds may react on undecomposed sulphide. The resulting metallic lead runs down the inclined hearth and collects in a basin, the SO₂ escapes into the flue, and the residue remains on the hearth. The temperature must remain low during this reduction period, so that the charge will not melt, but will remain in a pasty condition. The reactions are imperfect if the ore is melted.

It was found to be impossible to roast a large amount of lead ore uniformly in one operation in this manner. The first reaction that takes place on raising the temperature will not extract all the lead. The residue will contain rich PbS, with some lead oxide, lead sulphate, and lead silicate. The temperature is lowered, air admitted, and a second roasting takes place, followed by a second reduction. This cycle is repeated several times before the bulk of the lead is extracted. With each successive reduction, the temperature must be raised slightly, as the amount of lead diminishes. To counteract the melting of the charge, slaked lime is added. Toward the end of the process, there will not be enough PbS left to react on the PbO and PbSO₄, and to reduce these, coal is mixed in. Each successive operation is of shorter duration than the preceding one, and the metallic lead obtained is each time a little less rich in silver.

The products of reverberatory smelting are as follows:

1. *Lead.* If clean enough this can be rendered fit for market by simply liquating and poling; if it carries silver, arsenic, antimony, or copper, refining must be resorted to.

2. *Gray Slag.* This is a more or less matted mixture of lead (PbS, PbO, PbSO₄, PbSiO₃), gangue, cinders, and lime, with some silver. It is crushed and smelted in the blast furnace.

3. *Flue Dust.* This consists mainly of oxidized compounds and is worked in with subsequent charges, shortening the time required for roasting. If very impure, it is smelted in the blast furnace, with the gray slag.

4. *Hearth Bottom.* This consists of hearth material impregnated with metal. It is worked up in the same manner as the residues.

Limitations of Roast-reaction Process.—To be suited for the reverberatory furnace, an ore must be a rich galena, or a mixture of galena and carbonate, that does not contain less than 60 per cent Pb, 70 per cent being preferable. It may not contain more than 4 or 5 per cent SiO₂, and its content of zinc blende, pyrite, chalcopryrite, calcite, and barite must be low. The process takes heavy fuel and much skilled labor.

Classification of Reverberatory Methods.—Reverberatory procedure varies widely in different countries, three distinct methods of reverberatory work being recognized. Carinthian, English, and Silesian. Some of the principal plants work toward the object of extracting as much lead as possible in the reverberatory (Carinthian and English), while others supplement the reverberatory by the blast furnace, taking out only a major portion of the lead in the former. The rich residue from the reverberatory, smelted in the blast furnace, permits a higher total extraction (Silesian). Some establishments roast the ore slowly at a low temperature, thereby obtaining a maximum recovery of lead (Carinthian and Silesian), while others conduct a hurried high-temperature roasting, aiming to save time and labor at the expense of metal (English). Reverberatory furnaces vary in form and size also.

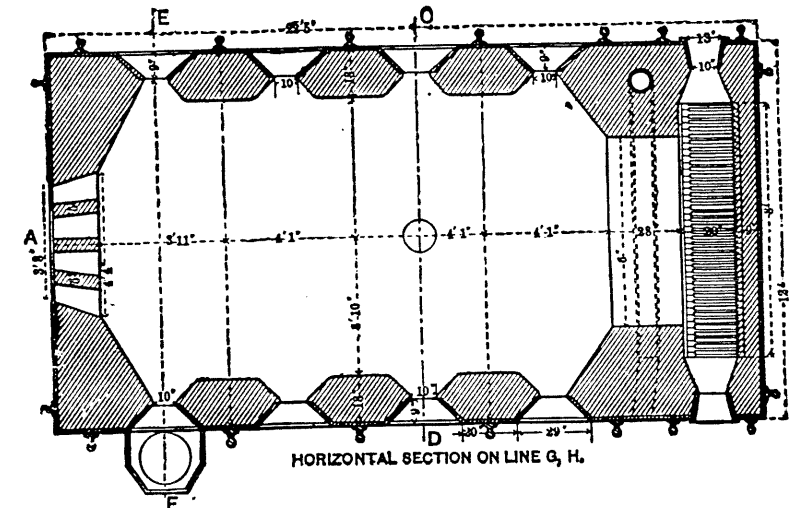
The Carinthian method is distinguished by the smallness of the charge, slow roasting, low temperature of all operations, and the extraction of all the lead in the reverberatory. The hearth is inclined toward the flue and the lead collected outside the furnace.

The English method is marked by a large charge, quick roast, high temperature throughout, and extraction of all the lead in the reverberatory. The hearth slopes

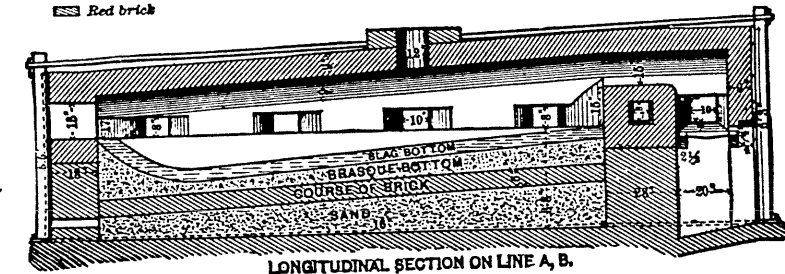
toward the middle of one of the sides, and the lead collects inside the furnace, being tapped at intervals into an outside kettle.

The Silesian method is characterized by a large charge, slow roasting, and a low temperature, the lead being only partly recovered in the reverberatory, which is supplemented by the blast furnace. The hearth is inclined toward the flue, beneath which the lead is collected and tapped at intervals into an outside kettle.

The Silesian furnace (Tarnowitz) is shown in Figs. 7 to 9.



Fire brick
Red brick



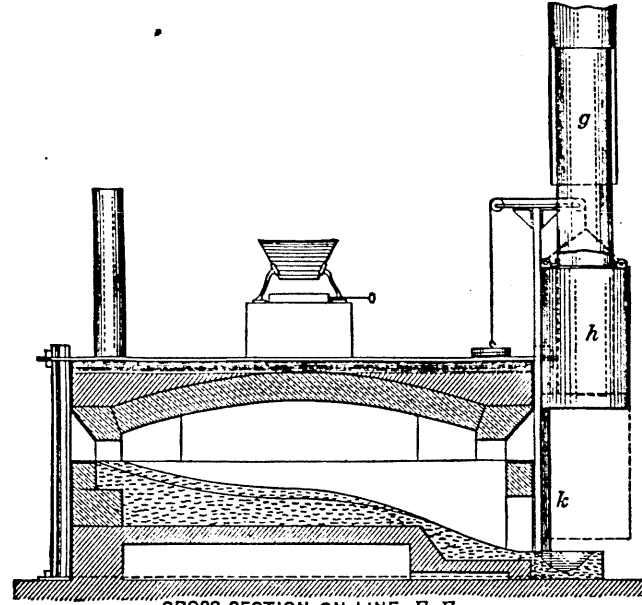
FIGS. 7-8.—Silesian reverberatory furnace.

Smelting Lead Ores in the Ore Hearth.—The ore hearth has come back into an important position in the lead industry during the present century. It is an ancient method, with operating principles that may be said to be intermediate between a reverberatory and a blast furnace. At first the only method for working low-silica high-grade galena ores, it passed into disuse and became largely replaced by the reverberatory furnace, but the reverberatory has given way, with the advent of the baghouse and Cottrell electrostatic processes for the collection of fume and dust, and the ore hearth, in modern mechanical form, has taken a new lease of life. In 1914, there were in operation in Missouri alone 75 ore hearths (hand operated) with an annual capacity of 230,000 tons of galena concentrate; by 1923, the Newnam mechanical ore hearth had replaced all the hand hearths on the American continent;

about fifty of these furnaces were in operation in 1941 with a capacity of 500,000 tons annually.

Plants have also been erected, and are at present in operation, in Canada, England, Spain, and South America, treating not less than 60,000 tons.

An ore hearth is, essentially, a low fireplace surrounded by three walls, with one or more tuyères at the back. It is invariably made of cast iron. In the front there is a cast-iron "work plate," with a groove to carry off the reduced lead into a kettle. There is usually a partial front wall composed of a thick bar of iron, but often the front is simply a dam formed of ashes and powdered galena which is impervious to melted lead. The sides and back must be of iron in order to admit of chipping off



CROSS SECTION ON LINE E-F
FIG. 9.—Silesian reverberatory furnace.

the half-fused masses of slag that constantly adhere to them; they may be cooled simply by radiation from large heavy castings (Scotch hearth), by a current of air (Rossie hearth), by a water box (American water-back hearth), or by both air and water boxes combined (Moffet-Jumbo hearth). These differences may conveniently be taken as indicating the four distinct modifications of the hearth process, though the manipulation is much the same in all. The Newnam mechanical hearth, water-cooled, is, of course, a fifth type.

The process carried on in the ore hearth is mainly the roast-reaction process, resembling that of the reverberatory furnace, but differing in the respect that roasting and reduction go on simultaneously and that there is considerable direct reduction of lead oxide to metal by the carbon of the fuel. The charge—ore and fuel—floats on a bath of molten lead; the PbO and PbSO₄ react on undecomposed PbS; some PbO is reduced by C; and the metallic lead trickles through the charge to the bottom, overflowing into an outside kettle.

The character of the ore to which the hearth process is adapted is determined by much the same limitations as for the reverberatory furnace. These limitations,

TABLE 3.—EXAMPLES OF SMELTING IN REVERBERATORY FURNACES

Items	Carinthian method				Silesian method			English method			Silesian method	
	Raibl, Carinthia	Engis, Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiperstones, Shropshire	Delege, Missouri	Tarnowitz, Silesia	Old furnace	New furnace	
Hearth, length.....	11'	6' 6 1/2"	9'	9'	10'	12'	9' 9"	16'	11' 9"	16'	16'	
Hearth, width at bridge.....	5'	4' 3 1/4"	3' 2"	3'	3' 6"	3' 6"	4'	11'	10' 10"	8' 10"	6'	
Hearth, width at middle.....	5'	4' 4 1/4"	3' 2"	3'	4'	9' 6"	9' 6"	11'	10' 10"	11'	8' 10"	
Hearth, width at flue.....	1'	3' 3 1/4"	3' 2"	3'	2'	4'	3' 3"	8"	10' 10"	8"	4' 4"	
Hearth, thickness of bed.....	6"	1' 5 3/4" - 2' 8 1/4"	6"	6"	6"	2' - 10" - 26"	4" - 18" - 30"	8"	10' 10"	8"	4"	
Hearth, life of bed, weeks.....	4-5	6	13" F.	-F.	-F.	20" S.	24" S.	13	27 1/2" F.	13	13	
Hearth, inclination to flue or side.....	21" F.	17" F.	13" F.	-F.	-F.	4' 6"	4' 6"	8"	8"	8"	8"	
Grate, length.....	7'	3' 7 1/4"	5' 6"	6' 6"	3'	4' 6"	2' 6"	1' 3"	1' 3"	1' 3"	1' 8"	
Grate, width.....	1' 3 3/8"	1' 6"	3' 7 1/4"	2' 6"	2'	3' 9"	1' 4"	1' 3"	1' 3"	1' 3"	3'	
Grate, depth below top of bridge.....	1' 2 3/8"	3' 7 1/4"	8" - 30"	6"	21"	24"	24"	24"	24"	24"	28"	
Bridge, width.....	5 1/2"	1' 3 3/4"	30"	30"	24"	43"	48"	48"	48"	48"	72"	
Bridge, length.....	3' 7 1/4"	3' 11 1/4"	14"	6"	6" - 8"	12"	12"	12"	12"	12"	15"	
Bridge, height above hearth.....	4-5"	8 1/2"	14"	14"	6" - 8"	9"	10" 1	10" 1	10" 1	10" 1	12"	
Roof, height above bridge.....	9"	3' 8 1/2"	14"	14"	6" - 8"	16"	16"	16"	16"	16"	17"	
Roof, height above hearth at flue.....	12"	8 3/4" X 2' 3 1/2"	14"	14"	6" - 8"	16"	16"	16"	16"	16"	17"	
Flue (leading to chimney), size.....	1' X 1' 3 1/4"	8 3/4" X 2' 3 1/2"	8" X 12"	8" X 12"	13" diam.	13" X 10"	13" X 10"	13" X 10"	13" X 10"	13" X 10"	4 (15" X 20")	
Chimney, inside size.....	1' 8" X 1' 8"	1' 3" X 1'	12" X 12"	12" X 12"	13" diam.	10" X 10"	11" X 11"	10" X 10"	10" X 10"	10" X 10"	43" diam.	
Chimney, height.....	20'	1' 3" X 1'	12" X 12"	12" X 12"	13" diam.	3' X 3' 6"	3' X 3' 6"	3' X 3' 6"	3' X 3' 6"	3' X 3' 6"	55'	
Grate area, ratio to hearth area.....	1:6	1:5.25	1:2.0	1:1.66	1:5.4	1:8	1:6.6	1:6.6	1:6.6	1:6.6	1:7.3	
Grate area, ratio to section of chimney.....	1:0.14	1:0.47	1:2.0	1:1.66	1:0.13	1:0.93	1:6.6	1:6.6	1:6.6	1:6.6	1:10	

* Kemp, School of Mines Quarterly, 1887-88, IX, p. 212. † Height of roof above grate, 38".

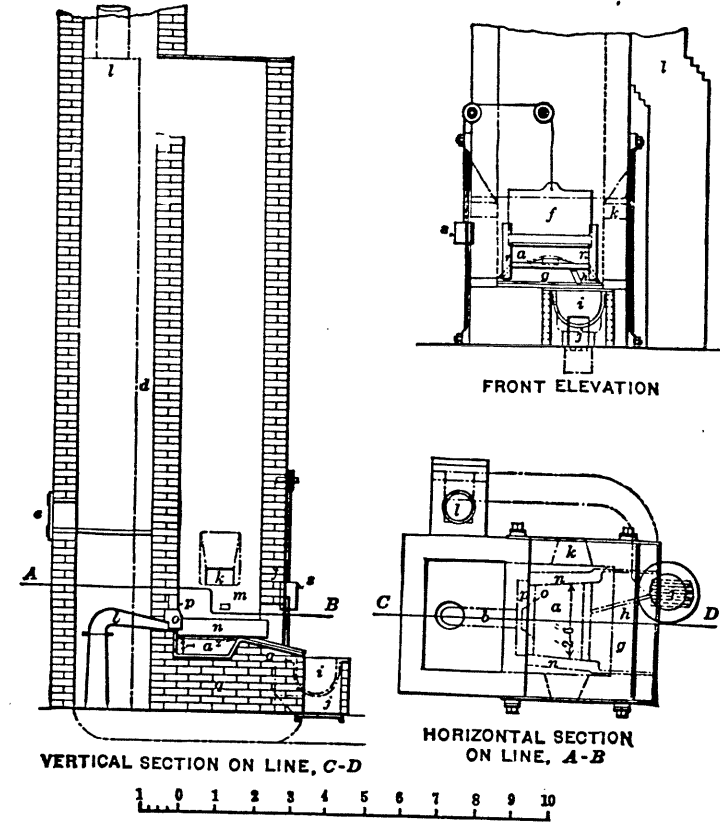
TABLE 5.—EXAMPLES OF SMELTING IN REVERBERATORY FURNACES.—(Continued)

Items	Carinthian method				English method			Silesian Method	
	Raibl, Carinthia	Engis, Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiperstones, Shropshire	Dealogue, Missouri	Tarnowitz, Silesia
Charge, weight in pounds.....	370-430	1,375	1,500	1,500	2,350	2,350	3,325	4,400
Charge, assay, per cent. lead.....	70	76	75-80	77.5	70	70-74
Operation, thickness on hearth.....	14"-14 1/2"	about 3"	1 1/2"	3 1/2"-4 1/2"	3"-4"	3"-4"
Men, number in 24 hr.....	10-12	12	12	9-11	6	7	8	12
Gray slag, amount in pounds.....	1.5	4	2	2	6	4	6	4
Gray slag, per cent. of charge.....	95	275	288	906	600
Gray slag, assay, per cent. lead.....	24	12	12	27	15
Of lead charged, recovered per cent., in bars.....	4	17-20	55	55	88	38	38.8
Recovered from gray slag and flue-dust.....	93	92.5	8	54.4	87.5
Total loss in lead.....	7	2.3	11	12	10	9.3
Outlay for labor, fuel and material per ton of ore of 2,000 lb. acid/100 parts	5.2	91	3.21
Labor, hours.....	90	61	36 aver.	20	15	12	8.4	11
Fuel, charcoal, pounds.....	1.10	0.8-0.9	0.46
Fuel, bituminous coal, tons.....
Fuel, wood, cords.....	1.60	1.10 aver.	0.83	0.57-0.76	0.56
Material, lime, pounds.....	26	20

¹ Includes smelting residue in the blast furnace.

Hofman.

however, are even more strict than for the reverberatory; the Pb content (usually 70 per cent) should not be less than 65 per cent, the ore should be coarser (necessitating preliminary pugging or agglomerating, if too fine), and only low-silver ores should be treated. This last restriction is due to the fact that much lead and silver is volatilized, under the blast of the ore hearth. With the development of methods of recovery of dust and fume in baghouses and Cottrell plants, these volatilization losses are, of course, greatly reduced.



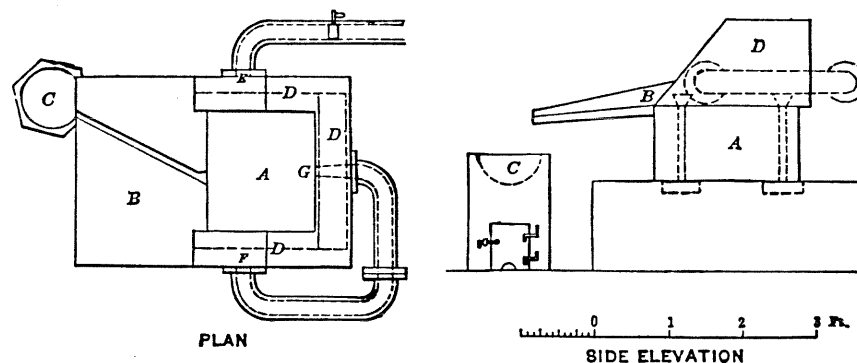
Figs. 10-11.—Hand-operated ore hearth (English).

The ore hearth has one great advantage over the reverberatory—it is quickly started and stopped, without much loss of fuel or heat, and is, therefore, adaptable to the intermittent extraction of lead from small amounts of nonargentiferous ore. It also consumes less fuel than the reverberatory, but requires purer and higher grade ore.

On the nonargentiferous high-grade lead ores of the Mississippi Valley, the mechanical ore hearth is almost supreme, although one large smelting plant remains still an advocate of the blast furnace as a method of primary treatment. The other major smelter reduces galena concentrate of about 70 per cent grade to bullion and gray slag on mechanical ore hearths, utilizing the blast furnace only as secondary equipment for the smelting of gray slag. Both methods are conducted with high efficiency, and the blast-furnace procedure has ardent advocates, but the high-grade

ore of the district is peculiarly adapted to ore-hearth treatment. On ore of 70 per cent grade, or better, a 65 to 70 per cent lead extraction is obtained, as bullion, on the hearth; if the concentrate is 80 per cent grade, a 90 per cent extraction, or better, is possible, coke requirements being 3 to 5 per cent breeze. Of the lead charged, 15 to 20 per cent is rehandled as baghouse dust and fume, but this is largely PbSO_4 and PbO , which is of immense assistance in the ore-hearth process, which depends on the interaction of galena with the oxide or sulphate to form SO_2 and precipitate Pb . If there were a sufficient amount of oxidized product present to oxidize all the PbS , it would be possible, theoretically, to reduce and recover all the lead in both forms with but little extraneous heat.

About 10 to 15 per cent of the lead goes into a 50 per cent product—gray slag—which must be re-treated, and which makes an excellent material for rapid, efficient blast-furnace smelting. The Collinsville, Ill., plant, as will be seen from the blast-furnace table, using Newnam mechanical ore hearths (and blast furnaces for auxiliary treatment), maintained an abnormally high smelting speed on its blast furnaces, 7.9 tons of charge per square foot of hearth (blast-furnace) area, owing to the easy smelt-



Figs. 12-13.—Rossie air-cooled ore hearth.

ing characteristics of gray slag which formed the principal constituent of its blast-furnace charge. On the other hand, it is to be noted that the Herculaneum plant with 80 per cent of its blast-furnace charge made up of Dwight machine double-roasted concentrate, and with no ore hearths or gray slag involved, has smelting speeds of 6.3 tons charge per square foot of blast-furnace hearth area. It has been found that the flotation concentrates of the Mississippi Valley, carrying 56 per cent lead, are not advantageously treated on the ore hearth, but must for maximum economy be double-roasted and smelted in the blast furnace.

The products of the ore hearth are similar to those of the reverberatory, with the added product of "browse," a mixture of ore, slag, and fuel, which goes back to the charge in the ore hearth.

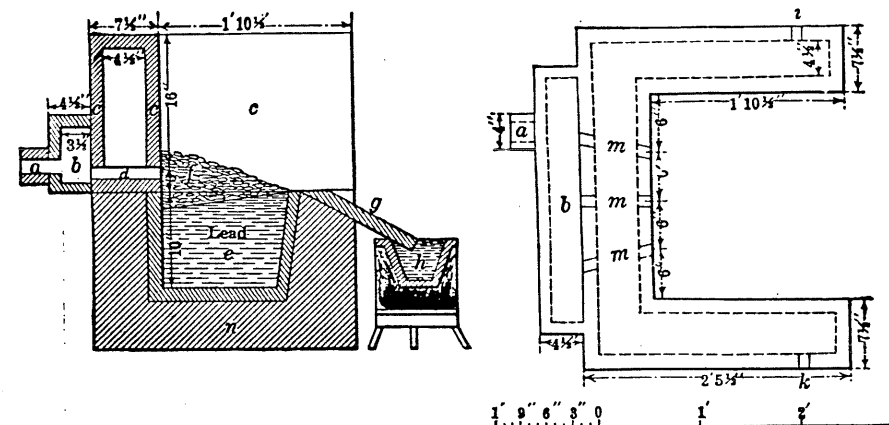
Being a simple type of metallurgical furnace, the ore hearth shows but little variety in construction or manner of operating. The four early hand-operated forms, shown in the accompanying illustrations (Figs. 16 to 20), differ somewhat radically from the mechanical furnace, the Newnam hearth, shown in Figs. 21 to 33.

Scotch Ore Hearth.—Figures 10 and 11 show a furnace used in England. The cast-iron box *a* set in brickwork *q* measures 2 ft. (front to back) \times $2\frac{1}{2}$ ft. (width). It is 1 ft. deep, and holds about 2 tons of lead. Work stone *g*, an inclined plate, is cast in one piece with the hearth box. Groove *h* leads the overflowing lead to kettle *i*, heated from fireplace *j*, the gases passing off through a flue into chimney *l*. On either

side of the hearth box is a cast-iron block *n*, and another iron block *o* is at the back. This back stone is perforated for the tuyère *b*, entering the furnace about 2 in. above the surface of the lead in the hearth. *p* is an upper back stone, or cast-iron block; the fore stone *m* is small. Brick shaft *c* carries off the fumes; at the back is a pit *d*, or dust chamber, cleaned through door *e*. On the side of the shaft is feed door *k*, for introducing fuel and removal of slag crusts at tuyères. Charge is fed from the front. A shutter *f* is in place at the front of the hearth; sliding in a frame *r*, it is raised and lowered by counterpoise *s*.

Bituminous coal is used as fuel. After operating for 12 to 15 hr. the hearth becomes too hot and must be cooled for about 5 hr. before work can be resumed.

The Rossie, or Air-cooled, Hearth.—Figures 12 and 13 show an arrangement of ore hearth in which the sides and back are air-cooled. The cast-iron jacket *D* has an air space inside. Blast enters at *E*, passes through *D*, leaves at *F*, and is delivered to tuyère *G*. This cools the walls of the hearth and preheats the blast. The Rossie



Figs. 14-15.—Original American ore hearth.

hearth could be used continuously, but the hot blast caused excessive volatilization, and this hearth was abandoned until recovery of fume became possible, when it was again brought into use.

Original American Water-back Ore Hearth.—Figures 14 and 15 show the water-cooled ore-hearth, in which work is continuous, owing to the cooling of the sides by water, which enters at *i* and passes out at *k*.

Modern American Water-back Ore Hearth.—In this furnace the cast-iron hearth box is supported by short columns in order to air-cool the lead; the upper sides are two water-cooled castings; the inside working length covers about 4 ft.; and two hoods are provided, an inner smaller one for carrying off dust and the bulk of fume by means of a suction fan, and an outer one for removing the remaining fume by natural draft. Such a furnace is shown in cross section (in Fig. 16).

Moffet Ore Hearth.—Figures 17 to 20 show the combined water- and air-cooled hearth, in double form, *i.e.*, two hearths placed back to back, under one hood. A water box cools the hottest part of the furnace, and upon this rests the air box, consisting of two separate chambers where the heated blast passes down through the water box by means of fourteen 1-in. copper tuyère pipes, seven on a side.

Newnam Mechanical Ore Hearth.—The hand hearths have all given way to the Newnam mechanically rabbled furnace, shown in Figs. 21 to 35. Figures 21 and 22

give a front and side elevation; Figs. 23 and 24, horizontal and vertical sections of the lead basin; Figs. 25, 26, and 27, elevations and sections of middle water jacket; Figs. 28, 29, and 30, elevations of right and left end jackets and section of right end jacket; Figs. 31, 32, and 33, details of cast-iron stand supporting the lead basin; and Figs. 34 and 35, perspective views of the furnace with rabbling mechanism at beginning and end of trip.

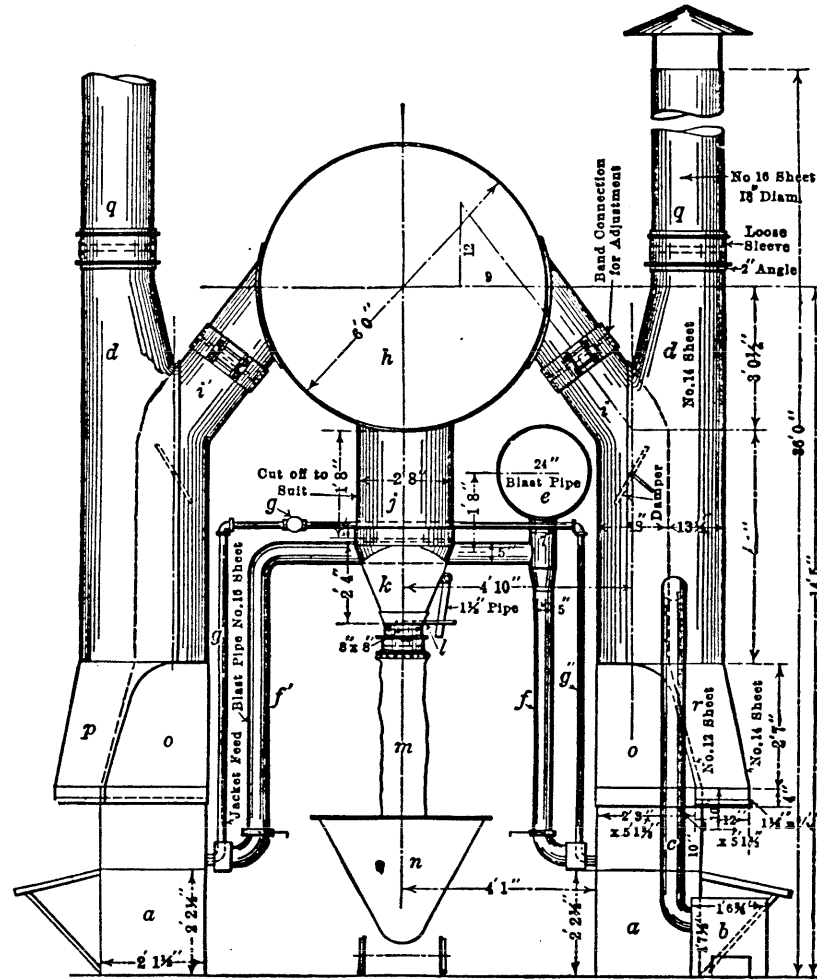
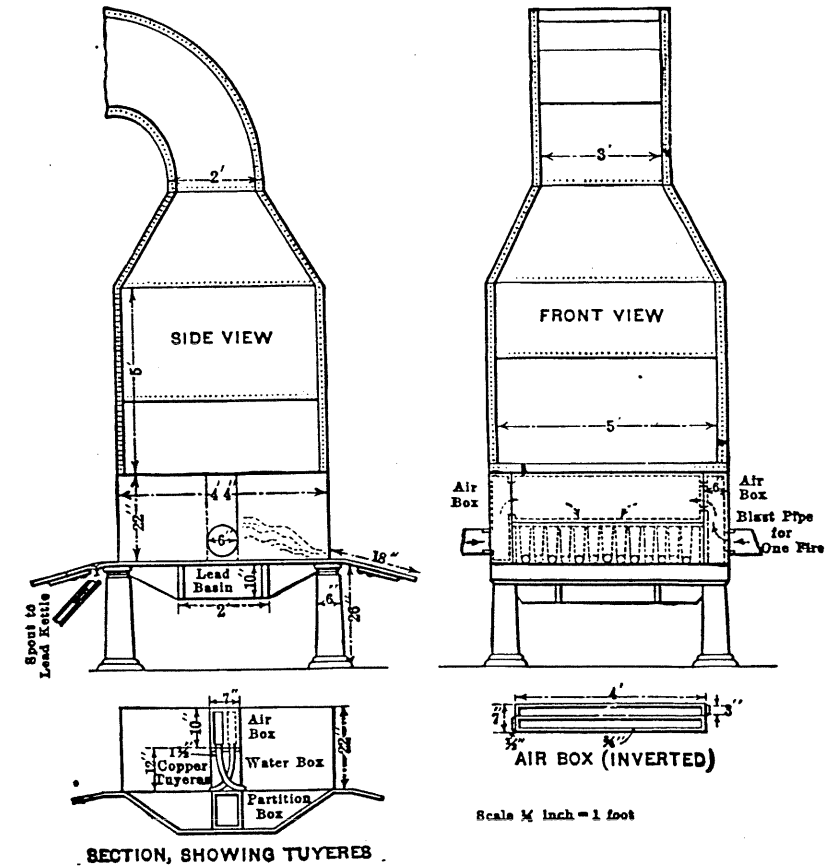


FIG. 16.—Modern American ore hearth.

The basin of the Newnam hearth shown is 8 ft. long, 19.5 in. wide at the top, 10 in. at the bottom, and 10 in. deep. The furnace has 12 tuyères. Lead discharges from the basin through siphon tap *e* (Fig. 23). The furnace is shown in perspective (Figs. 34 and 35), because the full assembly of detail drawings would be unnecessarily voluminous. The rabbling machine is hung from an overhead traveling carriage. This carriage starts from its position of rest at one end of the furnace. On the pulling of a lever, and during the trip to the other end, the rabble arm is given a motion similar

to that of the hand rabble. When the rabble arm is withdrawn from the fire, the carriage moves ahead 4 in. and starts the rabble on the next stroke. When the carriage reaches the opposite end of the furnace (Fig. 35), it is stopped automatically, the rabble arm withdrawn, and the carriage returned to its original position. A 1-hp. motor is sufficient for driving the axes of the carriage and the rabble arm.

The mode of operating with the Newnam mechanical hearth is the same as that in a hand-worked hearth, except that stirring is done by machinery. The first step in



SECTION, SHOWING TUYERES.

FIGS. 17-20.—Moffet ore hearth.

the normal working of an ore hearth is to spread a few shovelfuls of coal over the fire, and then a thin layer of ore mixed with 0.5 to 1.0 per cent lime. The fire is left undisturbed for a short time—1 to 1 1/2 min.—during which the charge is more or less oxidized, the flame breaks through, and the ore surface becomes crusted. The rabble arm thrusts over the edge of the basin into the lead and raises and loosens the slightly caked mass. As the mechanical arm rables the charge, one man follows it, pushes back the loose charge with a shovel, and drags the gray slag onto the apron plate. He is followed by a second man (charger), who transfers the gray slag to the water box, spreads a thin layer of ore onto the charge, and adds coke breeze as needed. By the time the trip to the end of the hearth has been covered, the ore first charged at the other end is ready to be rabbled.

TABLE 6.—EXAMPLES OF SMELTING IN THE ORE HEARTH

Name	Date	Furnace				Products				Materials					Ref-er-ence			
		Front to back	Width	Depth	Sides, kind	Tuyères	Ore in 24 hr., lb.	Lead in 24 hr., lb.	Gray slag in 24 hr., lb.	Per cent lead direct from ore	Men in 24 hr.	Bitu-minous coal, lb.	Coke, lb.	Peat, bu.		Char-coal, bu.	Wood	Lime, bu.
Rossie Works, N. Y.	1842	24"	24"	12"	Air-jacket	1	9,888	7,389	73.88	4	(a)	
Keld Head Mining Co., Eng-land	1870	23"	21"	12"	Cast-iron	1	10,752	8,064	602	74.44	6	374	(b)	
Leadhill & Warlock, Scotland	1895	22"	30"	6"	Cast-iron	1	6,720	6	500	(c)	
Wardale, England	1903	21"	27"	8-12"	Cast-iron	1	18,000	8,700	61.00	(d)	
Waulokhead, Scotland	1912	22"	30"	6"	Cast-iron	1	2,240	60.00	6	800	(e)	
Granby, Mo.	1877	22½"	24"	11"	Water-jacket	3	9,000	7,500	83.90	6	27.6	2.5	(f)	
Hopewell, Mo.	1877	22"	20"	12"	Water-jacket	1	6,000	1,464	73.20	6	(g)	
Lone Elm, Mo.	1889	22"	48"	10"	Water- and air-jacket	7	27,000	12,032	5,247	45.00	6	2,160	5.40	(h)	
Granby, Mo.	1908	15"	4'	10"	Water-jacket	4	14,000*	2,000	75.00	4	(i)	
Galena, Kans.	1909	5'	Air-jacket	10	21,000	50.00	6	(j)	
Granby, Mo.	1911	5'	Air-jacket	65.00	(k)	
Webb City, Mo.	1911	5'	7"	Air-jacket	10	14,000*	65.00	6	(l)	
Federal, Ill.	1914	18½"	4'	10"	Water-jacket	8	22,500	7,200	60.00	6	(m)	
Collinsville, Ill.	1914	18½"	4'	10"	Water-jacket	8	21,000	6,200	55.00	6	(n)	
Collinsville, Ill.	1923	19.5"	8'	10"	Water-jacket	16	52,000	24,400	9,000	67.00	6	(o)	
Joplin, Mo.	1916	20"	5' 5"	Air-jacket	28,000	12,600	4,200	60.00	6	1,200	(p)	
Galetta, Ont.	1917	19.5"	8'	10"	Water-jacket	16	56,000	33,000	8,000	75.13	6	(q)	

* = used
 * = works 12 hr. only
 * = Newnam mechanical ore hearth.

(a) *Am. J. Sc. & Arts*, 1842, xxii, 169; (b) *Fercy, "Lead,"* 278-283; (c) *Sexton, Eng. Min. J.*, 1895, lxx, 175; (d) *Middleton, Eng. Min. J.*, 1905, lxxx, 10; (e) *Correspondent, Can. Min. J.*, 1912, xxxiii, 678; (f) *Williams, "Industrial Report,"* p. 63; (g) *Ibid.*, p. 65; (h) *Dovey, Tr. A. I. M. E.*, 1889-90, xxiii, p. 874; (i) *Pekins, Eng. Min. J.*, 1907, xxxv, 388; *Buskett, Min. Eng. World*, 1908, xxx, 917; (j) *Brimmade, op. cit.*, 1909, xxxi, 1029; *Pulsifer, op. cit.*, 1914, xl, 450, 501; (k) *Brown, Tr. A. I. M. E.*, 1911, xiii, 402; *Pulsifer, Min. Eng. World*, 1914, xl, 450, 501; (l) *Ruhl, Min. Eng. World*, 1910, xxxiii, 1047; *Witch, Mines & Minerals*, 1911, xxxi, 709; (m) *Pulsifer, Min. Eng. World*, 1913, xxxix, 375; 1914, xl, 450, 501; (n) *Pulsifer, op. cit.*, 1913, xl, 450, 501; (o) *Newnam, Tr. A. I. M. E.*, 1916, lxx, 488; (p) *Brimmade, Min. Eng. World*, 1909, xxxi, 1029; (q) *Newnam*, 1924, correspondence.

greater in the Newnam than in the hand hearth, the work easier and more healthful, and the cost much less.

Data from leading ore-hearth plants have been assembled (by Hofman) as shown in Table 6.

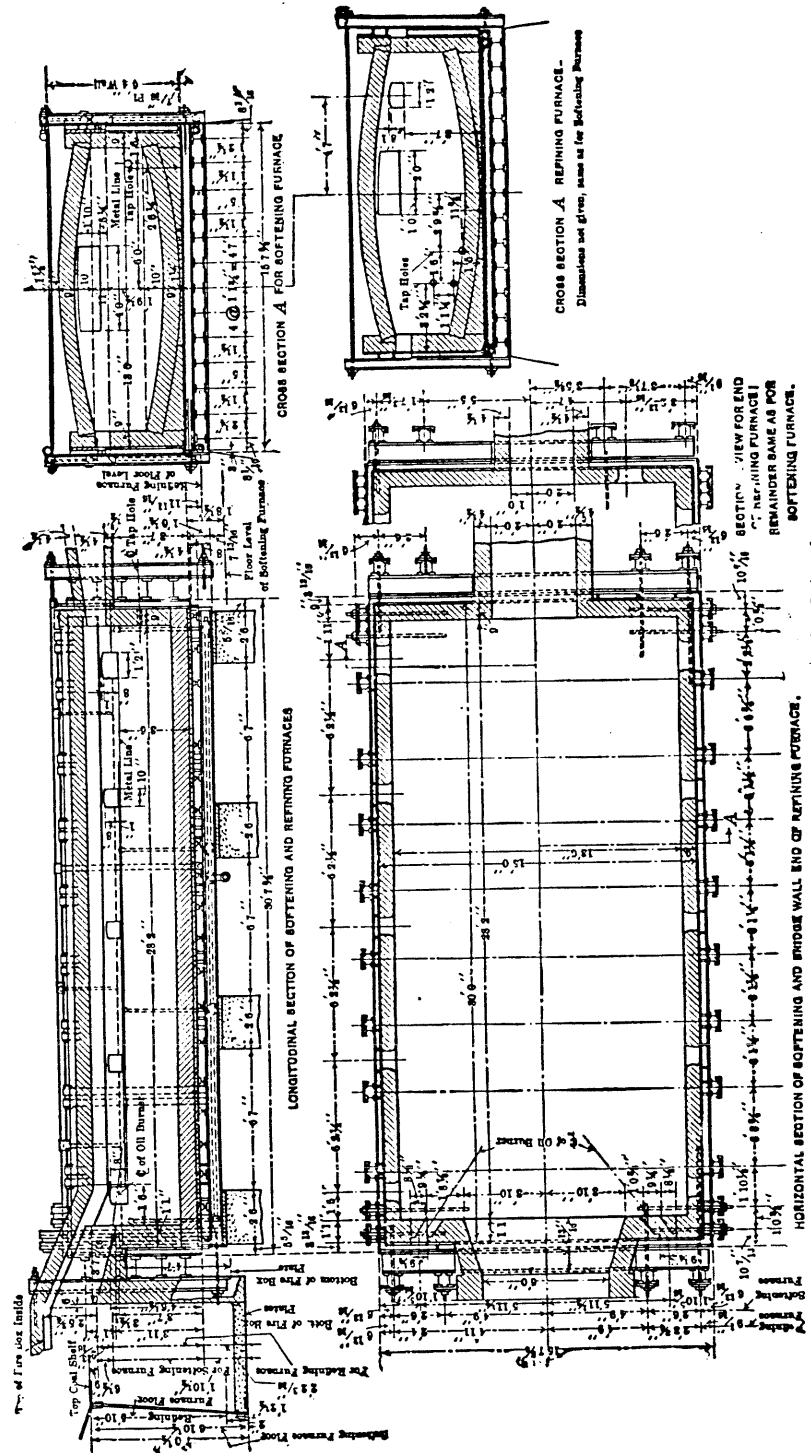
Desilverization and Refining of Lead Bullion.—The lead obtained from the ores of certain nonargentiferous districts—notably Missouri, Wisconsin, and a part of that from Spain and Germany—is comparatively free from silver as well as from base metals and can, therefore, be used in manufacture practically as it leaves the smelting furnace, after a simple "poling" or blowing with steam, followed by dressing. All the lead produced in blast furnaces from complex ores, however, contains at least enough silver to pay for extraction and, also, impurities which must be removed from the lead before it is fit for the market.

A desilverizing (refining) plant has for its task not only the separation of silver and the other precious metals (Au, Pt, Pd) from lead, but also the removal of the impurities Cu, Zn, Sn, Bi, As, Sb, S, Fe, Ni, Co, Te, and Se and the consequent concentration of a bullion carrying 95 to 98 per cent lead to a refined lead of not less than 99.73 per cent lead. These impurities themselves must also be worked up into salable products.

The standard methods of desilverizing and refining lead bullion are four in number: cupellation, Pattinson process, Parkes process, and Betts electrolytic process. Cupellation has ceased to exist as an independent process, but follows the processes of Pattinson and Parkes as an auxiliary. It can be adopted alone, however, in spite of its high losses and labor costs, for the treatment of rich lead in inaccessible districts where silver is the valuable metal sought. Up to the introduction of the Pattinson process argentiferous lead was cupelled; but costs and metal losses are so high that it is soon reached where the separation of silver by cupellation is not economical. The limit is at about 50 to 60 oz. silver per ton of lead. Below this grade, cupellation will hardly pay for the labor, fuel, and material used, the loss in the inferior grade of lead obtained from the subsequent reduction of the lead produced in cupellation. It becomes necessary, then, to concentrate the lead in a smaller amount of lead before cupeling, and this is done by the Pattinson process. The process of desilverization must be preceded by a complete treatment of the furnace lead for removal of copper, either by poling and cooling or by treatment with sulphur. This dressing is followed by a process of oxidation to remove metallic impurities. This oxidation is called "softening" in America and "improvement" in England. The Parkes process must be followed by a refining or dezinking operation to remove the zinc left in the lead by the process, and to remove small amounts of other impurities. Almost all the impurities in the furnace lead interfere, to a greater or less degree, with desilverization by either the Pattinson or Parkes processes. Generally speaking, the Parkes process requires a purer bullion than the Pattinson process.

Arsenic and antimony are the most troublesome impurities, even when present in small quantities. Next in order come tin, sulphur, iron, nickel, cobalt, and tellurium. Fortunately all these have a greater affinity for oxygen than lead and can, therefore, be largely removed by simple oxidation at a low red heat and a skimming of a molten bath.

Copper has less affinity for oxygen than the other impurities mentioned and is only partially removed by oxidation. It does form, however, an alloy with part of the lead itself, which is less fusible than pure lead, and resort is had to this characteristic to accomplish its removal in the ordinary dressing operation. Copper may be reduced to 0.002 per cent or less by treatment with sulphur, rapid agitation, and cooling to



Figs. 38-39.—300-ton softer and refining furnaces.

just above the freezing point of the lead. The copper is removed as sulphide with a considerable amount of lead in the form of a dry powdered dross.

Bismuth cannot be practically separated from lead by oxidation, as it has less affinity for oxygen than has lead itself. It does not interfere with desilverization but remains with the refined lead in the Parkes process. For most commercial uses of lead, bismuth is not an undesirable impurity; for some applications its presence in small amounts is very beneficial. For the production of white lead by the old Dutch process, however, its presence is undesirable, since it gives the product a gray color. The standard specifications for commercial grades (see page 145) limit the bismuth content of corroding lead, used for Dutch process white lead, to 0.05 per cent. Other commercial grades may contain up to 0.25 per cent bismuth. Removal of bismuth in the Pattinson process is not complete but is sufficient for some purposes. In the Betts electrolytic process, removal of bismuth is complete, since bismuth is not deposited on the cathodes but remains in the anode slime. Bismuth is reduced to 0.02 or lower economically by the Kroll-Betterton process by the use of magnesium and calcium as reagents.

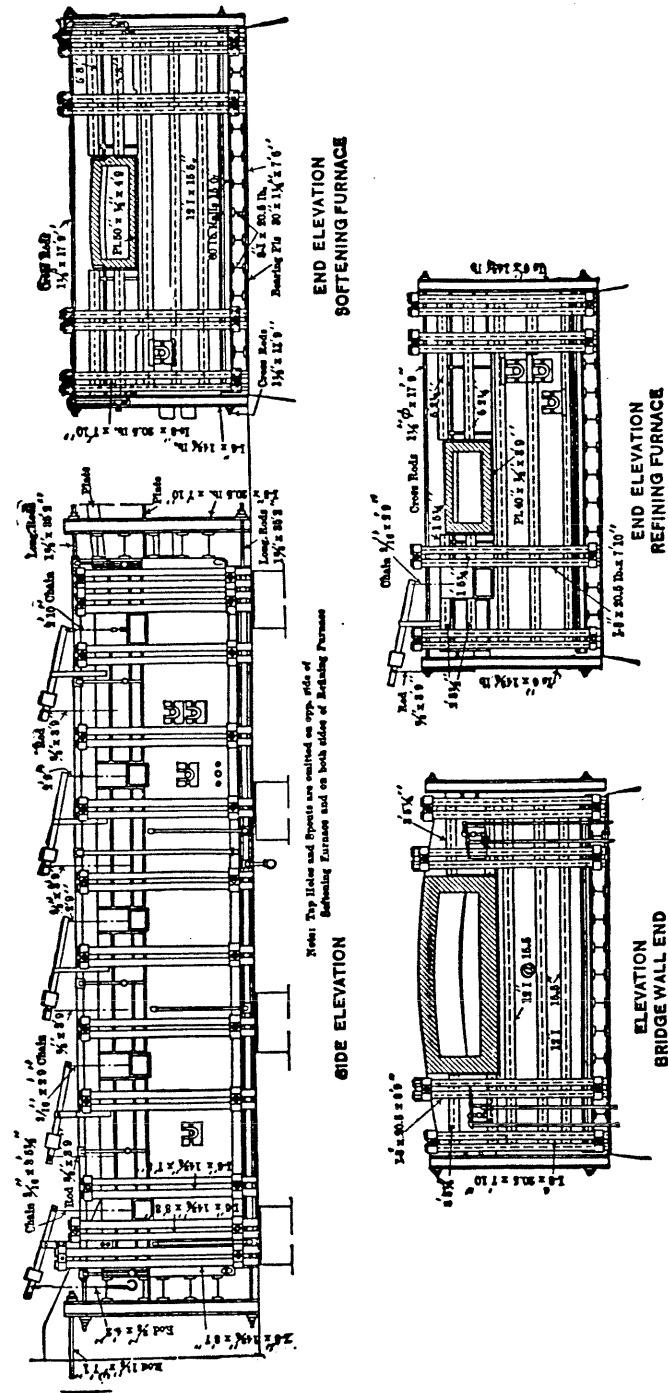
The many advantages that the Parkes process has over that of Pattinson have made it the preferred and most generally used desilverizing process in American practice. The Parkes method is lower in operating cost; produces market lead lower in silver content (0.10 to 0.20 oz. as compared with 0.40 to 0.60 oz. per ton by the Pattinson process); completely recovers even small traces of gold; produces a lead for cupellation with 2000 to 15,000 oz. silver per ton, as compared with 500 to 650 oz. by Pattinson; and shows a much lower loss of lead and silver.

A combination of the Parkes and Pattinson processes is sometimes used when bullion is high in bismuth, the desilverizing being performed by means of the Parkes process and the bismuth content of the desilverized lead being lowered by Pattinsonizing to 0.05 per cent, the dividing line between corroding and noncorroding lead. In more modern practice, combinations of the Parkes and the Kroll-Betterton process or the Betts process are used, which make it possible by combination of production to produce a range of bismuth content representing all commercial grades.

Softening.—The softening or "improving" of lead bullion as a preliminary to desilverizing by either the Parkes or Pattinson process is essential. This is partially accomplished in the dressing plants of lead blast-furnace smelteries which have no refinery on the premises and must therefore ship their base bullion to distant points for desilverizing. The major part of the softening operation is accomplished in any case at the refinery proper. In the Parkes process it has been shown that a decided saving in zinc consumption exists between the respective treatment of bullion that has been softened and bullion that has not been softened. For an unsoftened bullion containing 4.5 per cent foreign metals such as copper, arsenic, and antimony, 2.87 per cent zinc was required to desilverize the lead, whereas 1.75 per cent zinc sufficed if softening had preceded desilverization. The relative recoveries of market lead were 43 and 72 per cent of the bullion charged.

Softening has for its object the removal from the blast-furnace base bullion of the impurities that interfere with desilverization, mainly copper, tin, arsenic, antimony, and sulphur. Copper is best removed by a separate dressing operation prior to softening, but this operation is sometimes combined to some extent with the softening operation.

Furnace Softening.—The operation consists of two stages, liquation or dressing and oxidation. By liquation, metals held in solution by the furnace lead are separated from the lead by slow melting at a low temperature. By oxidation, which later occurs when the temperature is raised to a bright red with introduction of air or steam, metals alloyed with the lead are converted into oxides. These are to some



Figs. 40-43.—300-ton softening and refining furnaces.

extent volatilized, but mainly combine with the PbO, formed at the same time, and are slagged off.

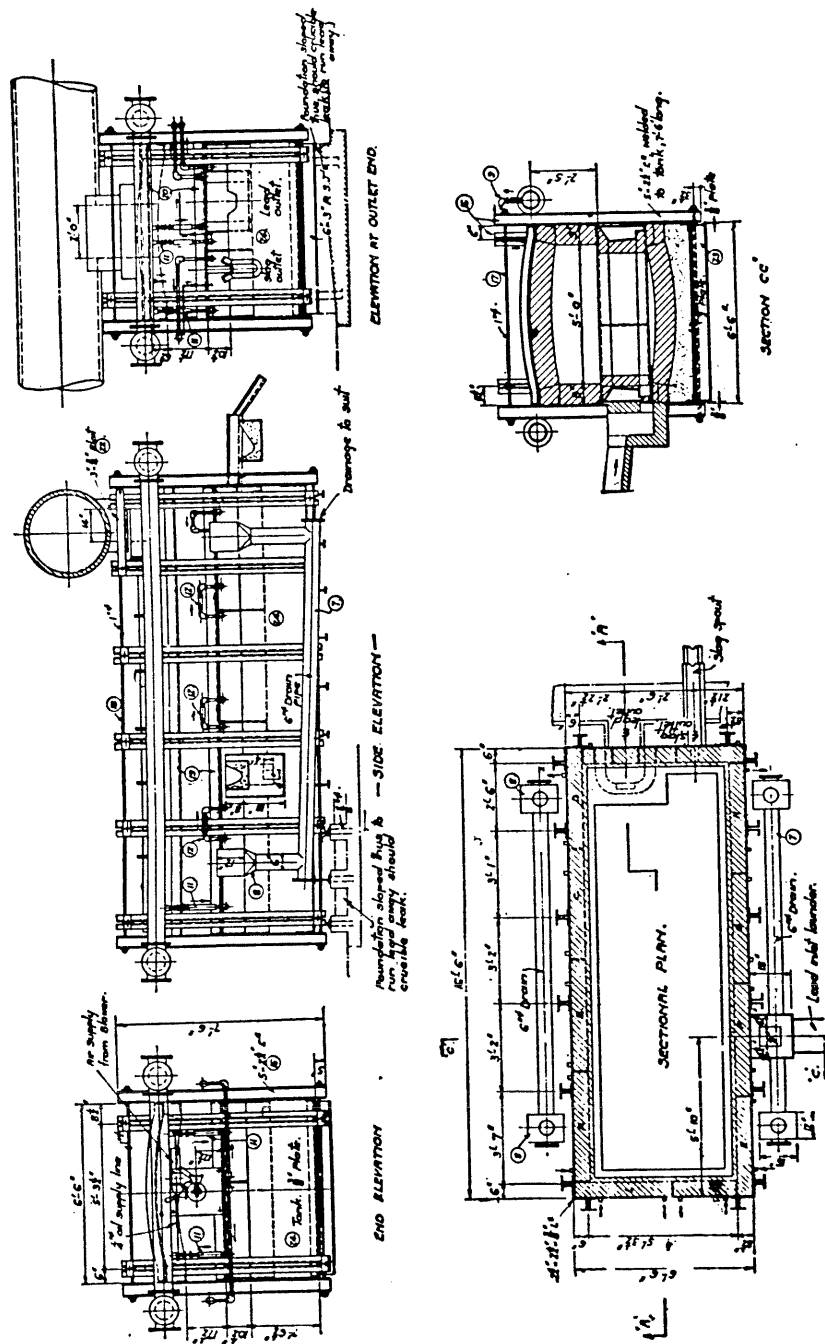
In the first step, the bullion is slowly melted at 370 to 380°C. and there rises to the surface a dross consisting principally of copper, sulphur, arsenic, and lead. In the second step when the temperature has been raised to a good red heat, the three principal impurities alloyed with lead are oxidized in the order tin, arsenic, and antimony. The surface of the bullion becomes coated with dark yellow powdery "tin skimming," mainly antimoniate and stannate of lead and antimoniate of tin. As soon as the tin skimming has been removed, the lead begins to give off fumes of arsenic and antimony, and arsenate and antimoniate of lead begin to form. These are drawn off together as an "antimony skimming" after the furnace has been cooled sufficiently to cause the skimming to solidify. The last traces of antimony come out with difficulty, and to hasten the process rich litharge from the finishing cupels can be stirred into the bath.

Jets of air or steam are introduced through perforated pipes, to stir the bullion and hasten the oxidation. Before the antimony has been removed, a sample of the bullion will "work," i.e., it will show small greasy particles of revolving black skimming on the surface of the lead. As the softening approaches the end point, these globules disappear and a thin yellow litharge forms.

In the continuous lead-refining process developed at Port Pirie, South Australia, discussed in more detail later, furnace softening is carried on continuously in a comparatively small water-cooled reverberatory furnace into which bullion containing 0.80 per cent antimony and 0.30 per cent arsenic flows at the rate of 26 tons per hr., and from which softened bullion containing 0.03 per cent antimony and 0.0004 per cent arsenic and a slag containing 8.0 per cent antimony flow continuously. The mixture of molten lead and slag flows continuously through a heated forehearth where the two separate by gravity and are withdrawn separately in a molten condition. The temperature of the softening reverberatory is maintained at 760°C. Air is introduced through water-cooled pipes submerged in the molten lead, and the oxidation reaction supplies the greater part of the heat required for the operation.

Three softening processes are in general use. Chemically the process is the same in each; however, the difference in equipment and operation is considerable. These are (1) batch-furnace softening, (2) continuous-furnace softening, and (3) Walker process or kettle softening.

In (1), a batch of 50 to 300 tons of molten bullion is held in a reverberatory furnace and agitated with air or steam at about 650°C. until the arsenic, antimony, and tin are lowered by oxidation to the desired amount. The temperature is lowered, and the oxides are skimmed off as a solid skim or semimolten slag. In (2), the molten bullion flows continuously through a small reverberatory heated to about 760°C. and is strongly agitated with air. The arsenic, antimony, and tin with some lead are oxidized to form a slag that is liquid at this temperature. The molten lead and slag flow continuously from the furnace to a heated forehearth where they are separated by gravity. In (3), the molten lead in batches of 100 to 250 tons is heated in kettles to about 675°C., covered with a layer of hydrated lime, and strongly agitated by mechanical stirring, or air is introduced below the surface. The arsenic, antimony, and tin are oxidized with some lead. The molten oxides are collected or "blotted" off by the lime, maintaining a clean metal surface for rapid oxidation. The oxide-lime mixture collects as a dry pelletized dust-free skim, which is skimmed off the surface of the lead. The metal of the kettle is protected by the use of lime from the corrosive action of the molten oxides of arsenic, antimony, and lead which would otherwise attack it at this temperature. This method may be applied to refining or dezinking lead with the same advantage, so far as protection of the kettle is concerned;



Figs. 44-48.—Details of softener, Port Pirie, Australian.

however, the amount of skimming produced is excessive, and the method has no economic advantage over other dezinking methods. As a softening method, it has proved very successful.

The furnaces used for softening and refining or dezinking in American practice are shown in Figs. 36 to 43.

The construction of the reverberatory furnace used for continuous softening at Port Pirie is shown in Figs. 44 to 59.

The fuel consumed in furnace softening ranges from 2 to 12 per cent, and averages 5 per cent soft coal, by weight, of the softened lead produced. Fuel oil is in some localities considerably more economical.

The time required for removal of arsenic and antimony by furnace softening varies with the size and design of the furnace, the temperature, the amount of air introduced, and other details of the operation. The rate of removal falls off as the impurity content is reduced. The total softening operation in practice includes of course the time of filling and emptying the furnace also. In general, it may be said that in a furnace of this capacity the complete softening of a charge of 200 tons of lead containing 1 per cent arsenic plus antimony will require 30 hr.

At Port Pirie a bullion containing 0.80 per cent antimony and 0.30 per cent arsenic is softened in the furnace illustrated at the rate of 26 tons per hr.

Colcord Process.—This process removes copper and arsenic from the bullion as the first operation in refining prior to softening. Sulphur is stirred into the metal with a mechanical stirrer at a temperature of about 350°C., which is sufficient to cause the sulphur to unite with the copper. The temperature is then raised to about 400°C. until the copper sulphide readily separates as a dross. The next step is to add caustic soda to the metal, raise the temperature to between 500 and 600°C., and thoroughly stir the caustic soda into the metal, using a mechanical stirrer, air jet, or other mechanical means. Arsenic contents of the metal can be reduced to any desired quantity by fractional additions of caustic. The sodium arsenate in the caustic skim is suitable for the manufacture of insecticides by leaching with water. The leached residue, containing lead and a little antimony, can be readily treated.

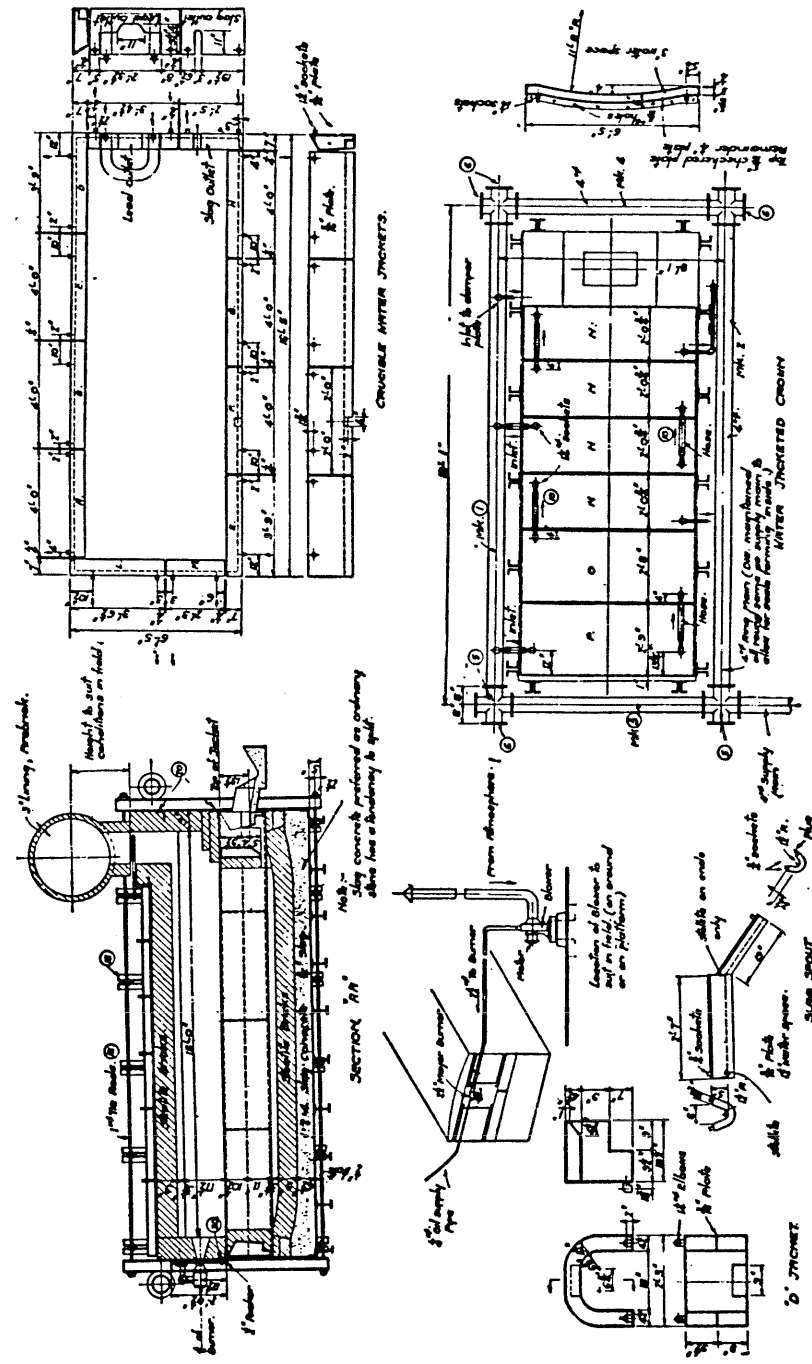
Arassic removed Nach Koh

After the softening operation, the bullion goes to whichever desilverizing process is provided and the desilverized lead must then pass to a refining or dezinking treatment for the removal of the zinc remaining from the Parkes process (0.55 per cent), as well as the small amounts of arsenic and antimony that may not have been entirely removed during the softening or that were introduced with the zinc used in desilverizing. If the desilverizing has been by means of the Pattinson process, refining is sometimes necessary to remove the arsenic and antimony retained in the crystallized lead.

Harris Process.—The Harris process of softening and dezinking by the use of sodium hydrate is now in use at refining plants in England and on the continent, in Mexico, and in North Africa. This process is applicable to softening or dezinking of desilverized lead. It thus both precedes and follows the standard desilverizing operation by either the Parkes or Pattinson process.

The process is designed to accomplish the removal of such impurities as arsenic, antimony, and tin from base bullion or any other metallic lead material, and the removal of zinc from desilverized lead.

This is done by bringing about an intimate contact between the metal, at a temperature not greatly in excess of its melting point, and molten sodium hydrate. A clean separation takes place, thereby, of the lead from its impurities, arsenic, antimony, tin, and zinc, which are quantitatively collected in the form of their oxides or oxysalts, suspended in or otherwise associated with the molten caustic. The mixture of caustic and oxide is then treated by a wet process for the recovery of the contained



FIGS. 49-59.—Details of softener, Port Pirie, Australia.

reagents and of the oxides and oxysalts derived from the impurities removed from the lead.

The circuit of the wet process is closed and complete, rendering a recuperation of 95 per cent of the free reagents possible, which, in turn, are used again in the process. The impurities are also completely and separately recovered and are free from either lead or other impurities. Arsenic and zinc, the latter from desilverized lead, are directly obtained in salable form, the former as calcium arsenate, the latter as zinc oxide, while the recovered antimony and tin compounds can readily be reduced to metal. The essential feature of the Harris process is that a clean separation of the constituents of the bullion is made possible, each being recovered completely and in marketable form. The operation is all performed in, and above, the regular refinery kettle, without furnaces. The pumping apparatus and chemical-treatment tank is a portable unit which is swung onto the top of the kettle and removed when purification is complete.

In the usual design of this apparatus the molten mixture of caustic and other salts is contained in a small tank through which the molten lead is pumped and allowed to overflow and return to the kettle. The circulation of the lead through the molten reagent is continued until the desired purity is obtained.

The process is sound and practical in principle and has many advantages, but has not been universally adopted, since in practice it cannot always compete economically with other processes. Where it has been successfully applied, considerable modification has been necessary in most cases to adapt it to local conditions and materials.

Furnace Refining.—The furnace used for dezinking and refining is similar in construction and operation to the softening furnace, except that a higher temperature is required. The furnace is filled with desilverized lead containing 0.55 per cent zinc at a temperature of 450°C. The temperature is raised rapidly to 750°C., and steam is introduced through submerged pipes. The steam aids the oxidation by agitation and also by the decomposition of water by metallic zinc. The treatment is continued until the zinc and antimony are reduced by oxidation to approximately 0.001 per cent zinc and 0.005 per cent antimony. The zinc and antimony, with considerable lead, are skimmed from the surface of the molten lead in the furnace in the form of a dry powdery oxide skim, which changes to a molten slag at the end of the operation. For a lead containing 0.55 per cent zinc and 0.3 per cent antimony the operation requires 12 to 16 hr. and produces about 5 per cent skim, containing about 90 per cent lead. Corrosion of the furnace refractories by the refining skim is very severe.

Dezinking with Chlorine.—The chlorine dezinking process is the one most generally employed in the lead refineries in the United States. It has the advantages that the destructive corrosion of the refinery equipment is avoided and the zinc is recovered in a marketable product. The process is conducted in kettles using any one of several types of apparatus. One of these, the Betterton apparatus, is shown in Fig. 60.

The molten desilverized lead is heated to 450°C. in a kettle and is pumped through a chamber where it is brought into intimate contact with gaseous chlorine. The zinc contained in the lead is converted into zinc chloride, which separates from the lead and floats as a molten layer on the surface of the metal. The molten zinc chloride is removed from the surface, cleaned by treatment with metallic zinc, and marketed as a commercial chemical. The dezinked lead must be given a further treatment to remove antimony. This is done either by oxidation in a reverberatory furnace or by treatment with sodium hydrate in a kettle.

Molding Refined Lead.—Refined lead was formerly ladled by hand from the kettle into molds placed in front of it. This operation is now performed by mechanical equipment. The refined lead is run into molds either directly from the reverberatory

or kettle in which the zinc and antimony have been removed from the desilverized lead, or, as is more common practice with plants having large units, the refined lead is tapped into a storage reverberatory furnace or market kettle from which it is run or pumped into molds. The storage reverberatory is of the same capacity as the refining furnace, and its construction is similar, though it is not generally water jacketed.

A great variety of mechanical casting machines for pig lead have been developed and are in use. Each type is usually a local modification of a standard type, though some designs have become standardized and are sold by equipment manufacturers.

The three general types are the "straight line" or Walker type, the "vertical wheel" or Miller type, and the "horizontal wheel" or Newnam type. Much ingenious mechanical equipment has been developed for performing the various operations of skimming, trimming, stamping, and handling of the bars, and the labor required for the molding operation has been greatly reduced. With machines molding an average

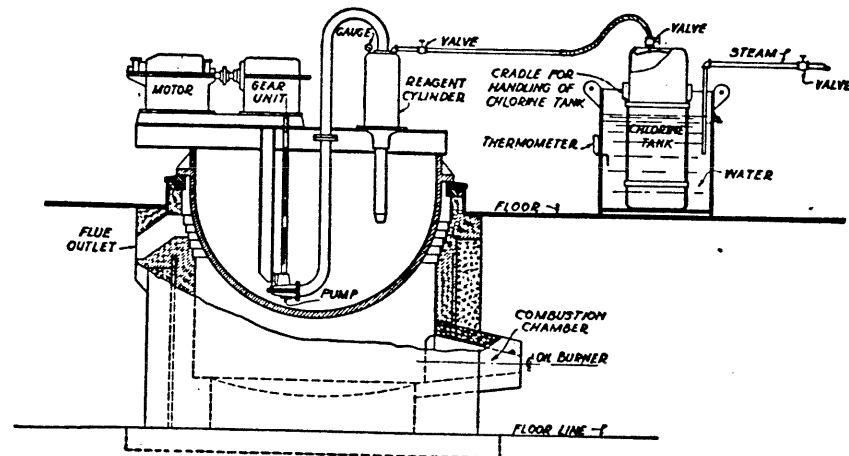


Fig. 60.—Betterton chlorine dezinking machine.

of 35 to 50 tons per hour, lead can be molded, weighed, and placed in stock or in cars for shipment with a crew of four men, one of whom operates a power truck.

Straight-line Molding Machine.—The lead is usually run from the furnace or pumped from a kettle through a pipe, provided with a regulating valve, into a cast-iron trough which tilts on trunnions. The side of the trough has a number of 1-in. spouts through which the lead flows into the molds when the trough is tilted by means of an air lift, thus pouring a number of bars, usually five, at one time. The molds are carried by an endless link-chain conveyer which travels in a horizontal direction in front of the pouring trough. The conveyer travels for a distance beyond the trough, where the lead in the molds may be skimmed by hand. The bars are then cooled in travel by water sprays from below and are trimmed and stamped by hand or by mechanical devices. The conveyer then passes up an incline and discharges the bars by inverting the molds. The bars fall onto a table or truck and are stamped and handled either by hand or mechanically. While some horizontal straight-line machines have been designed to start and stop, traveling each time the distance represented by a group of bars poured, this slows the operation of the machine and introduces mechanical difficulties in preventing vibration and roughening of the molten lead in the molds. For this reason the conveyer usually travels continuously, and the pouring trough is arranged to travel with the conveyer while pouring and to be returned to its original position at twice the normal speed by an automatic mechanism.

Vertical-wheel Machine.—The Miller casting machine consists of a vertical iron wheel with water-jacketed molds on its periphery. This machine handles 12 to 14 tons of lead per hour with three men.

Horizontal-wheel Machine.—The Newnam casting machine is a horizontal-wheel type of machine that handles 50 tons of lead per hour with four men. The molds are arranged in sets of five parallel pigs, supported radially on a horizontal-wheel structure. Five pigs are poured simultaneously. As the wheel revolves the pigs are cooled, trimmed, and passed under an automatic stamping machine. They are removed by a pig-pulling and stacking machine which lifts the pigs out of the molds in sets of five and places them in a stack of 35 weighing approximately 3200 lb. The

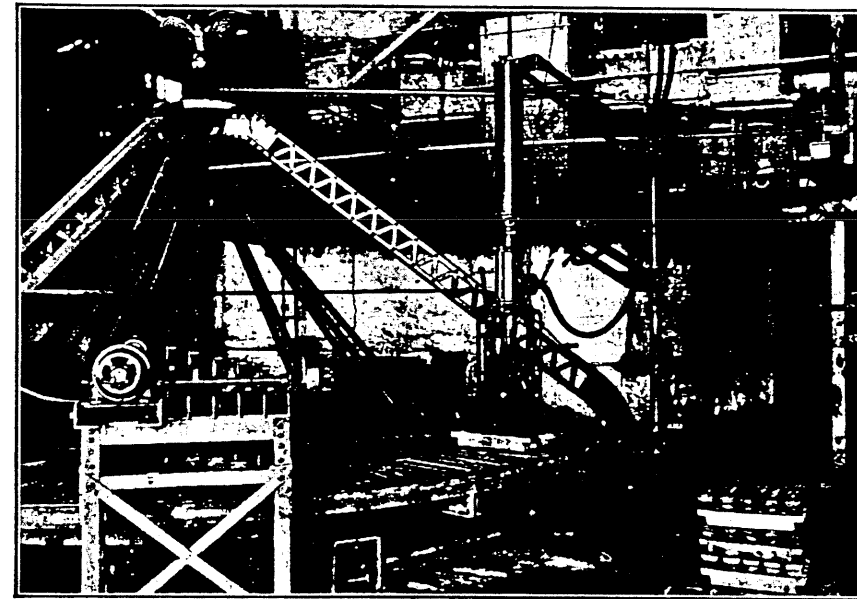


Fig. 61.—Five pigs just being lifted by Newnam pig-pulling and stacking machine.

stack is picked up by an electric truck of special design which, after passing over the scale, places the pile in stock or in a car for shipment.

The Newnam machine and lead truck are illustrated in Figs. 61 to 63.

Parkes Process.—This method of separating silver from lead is based on two facts: (1) a greater affinity of silver for zinc than for lead, and (2) the insolubility of zinc-silver alloys in lead which is already saturated with zinc. The process consists, in brief, of stirring 1 to 2 per cent of zinc into a bath of molten lead heated to above the melting point of zinc (415°C.) and allowing the mixture to cool, whereupon a crust rises to the surface of the molten lead containing nearly all the silver. A repetition of the zinc addition, in smaller quantity, gives another, lower, silver crust and leaves a molten lead that is practically free from silver, containing usually not more than 0.20 oz. per ton.

The zinc crust, which contains considerable lead besides the zinc and precious metals, is distilled in retorts for the recovery of zinc and to obtain an enriched retort bullion, which is cupelled to produce doré silver, with litharge as a by-product.

In addition to combining with silver, zinc has an affinity for other metals present, notably gold and copper, with both of which it combines before picking up silver.

The desilverizing operation proceeds as follows: When the softened bullion in the kettle has been drossed and brought to about 482°C., blocks of crust from the preceding second zinking are charged and sufficient new zinc also is added. In some plants the blocks from the second zinking are charged first into the empty kettle, melted, and then the spelter added; following this the bullion is tapped into the kettle from the softening furnace and the mixture stirred to incorporate the zinc. In any case the crust and spelter must be incorporated into the bullion and the zinc brought into intimate contact with the metals gold, silver, and copper by thorough agitation. In some plants a small amount of ammonium chloride is thrown into the kettle before

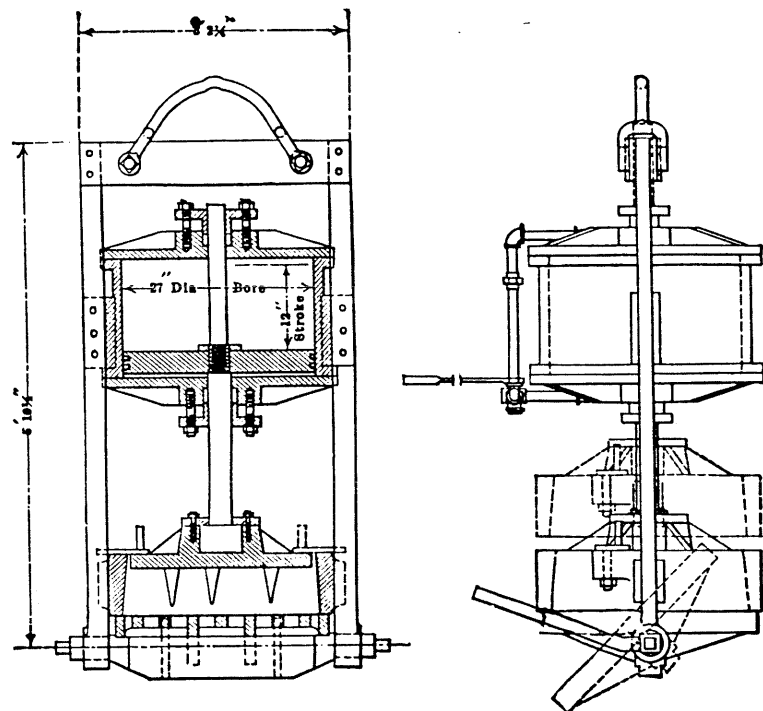


FIG. 64.—Howard press.

stirring (about 1 lb. to 10 tons of lead) for the purpose of keeping the tools clean and counteracting the oxidation of crusts. Except in very small operations, hand and steam agitation have been replaced by mechanical stirring, using the Howard mixer. This consists of a motor-driven propeller carried on a vertical shaft and supported at the center of the kettle on a removable bridge. The depth of immersion of the propeller varies in different plants and in some designs is made adjustable. In the original design of this mixer, the propeller was surrounded by a sheet-steel cone or cylinder open at top and bottom. In some designs this element is eliminated. The propeller is rotated to produce a downward flow of metal, and in operation a vortex is formed in the molten lead at the center of the kettle about the mixer shaft and a very thorough turning over and mixing of the metal is produced.

After stirring for 10 to 30 min. the first crust is removed and pressed. The second addition of zinc is then made and stirred in. The first crust is removed without lowering the temperature, which is held at about 450°C. since it is desirable to remove as

little lead as possible with the crust, and there is no attempt to clean the remaining lead of silver. In skimming the second crust, the temperature of the lead is lowered until all the crust that can be made to do so rises to the surface and is removed.

The weight of the crust produced varies with the amount of silver pressed. On a 100-ton kettle with 100-oz. bullion the first crust weighs approximately 7000 lb., and the partly desilverized remaining lead will contain 40 to 60 oz. of silver per ton. The second crust will weigh approximately 25,000 lb., and the desilverized lead remaining will contain less than 0.2 oz. of silver per ton. Two men in addition to the kettle

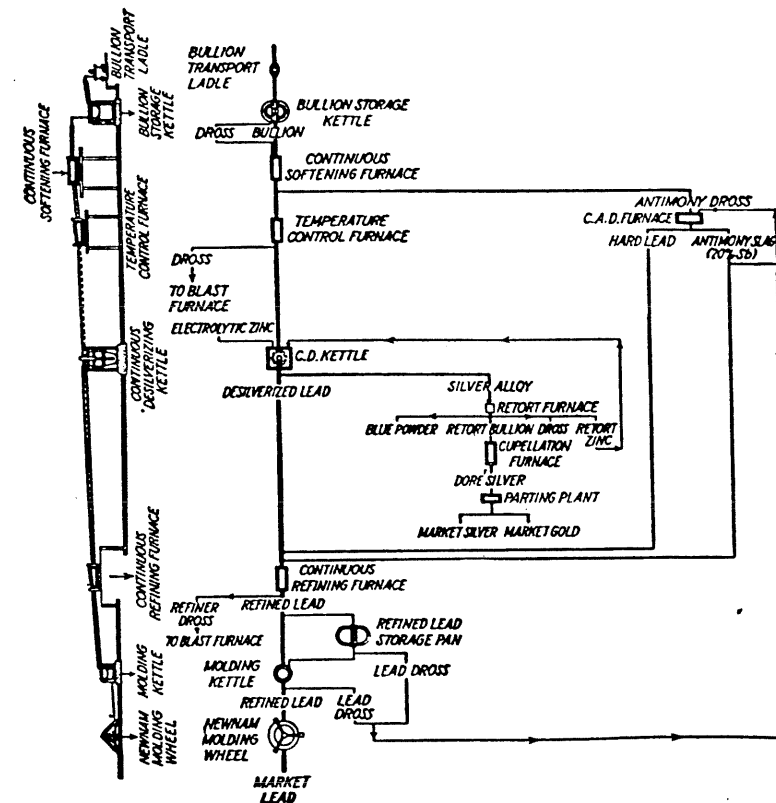


FIG. 65.—Flow sheet of continuous refining.

firemen usually do the entire work of desilverizing a single kettle of lead. About 2 tons of coal per 8-hr. shift is consumed.

Continuous Lead Refining.—At the Port Pirie plant of the Broken Hill Associated Smelters Proprietary Ltd., the operations of furnace softening, desilverizing by the Parkes process, and furnace dezinking have been combined and reduced to a continuous process in which the bullion flows continuously through these steps in succession and emerges completely refined. Slag, drosses, and other by-products are also withdrawn continuously and re-treated. A flow sheet of the process is shown in Fig. 65.

The softening furnace, briefly described under Furnace Softening, is a rectangular water-jacketed reverberatory fired with oil. The bullion enters and leaves the furnace

through submerged trapped openings. Molten slag overflows from the furnace continuously. Air is introduced through two water-cooled submerged blowpipes. The brickwork is of steatite bonded with sodium silicate.

Analyses of feed and products are shown in Table 7.

TABLE 7.—PORT PIRIE CONTINUOUS SOFTENING

Material	% Sb	% As	% Cu	Ag, oz.	Au, oz.
Drossed bullion to furnace.....	0.78	0.29	0.004	53.1	0.039
Softened bullion from furnace.....	0.03	0.0004	0.004	54.0	0.040
Molten slag from furnace.....	8.10	2.70	0.005		

The desilverizing kettles are of deep narrow form, resembling a bottle in cross section. They are approximately 20 ft. deep and 10 ft. in diameter at the widest point. Means for differential heating at different points in the kettle are provided in the setting, and definite temperature zones are maintained at different depths. The kettle is kept full of molten metal at all times. A practically constant range of composition and temperature is maintained from desilverized lead at 350°C. at the bottom to a layer of rich silver-zinc dross at 650°C. which floats on the surface. The molten softened bullion flows continuously to the kettle, entering at a temperature of 650°C. It passes downward through the zinc dross and various layers of molten metal, losing its silver content in the passage, and is withdrawn continuously from the bottom of the kettle through an inverted-siphon discharge pipe.

The silver-zinc dross is ladled out of the top of the kettle, concentrated in a liquating kettle similar in design to the desilverizing kettle, and is retorted and cupeled in the usual manner. The desilverized lead flows continuously to a rectangular reverberatory furnace similar to the softening furnace, is dezinked by oxidation, and flows continuously to a Newnam molding machine.

The continuous process requires a constant supply of bullion of uniform composition and produces a uniform product. It has the advantage of compactness in plant design, small stocks of by-products to be stored, and economy of labor required.

Equipment Used in the Parkes Process.—The kettles used in lead-refining operations may be constructed of cast iron, cast steel, or welded steel. They are usually of approximate hemispherical form and occasionally are elliptical. They range in capacity from 30 to 300 tons. Kettles up to 30 tons in capacity are usually made of cast iron. Larger sizes were formerly cast but in modern practice are made of welded steel plate up to 2 in. in thickness. The steel construction has the advantage of a thinner wall for heat transfer and also the fact that cracks or flaws may be repaired by welding, giving the kettle a long life in service.

Howard Stirrer.—The Howard stirrer or mixer is used for agitating molten lead when introducing zinc in the Parkes process or other reagents used in refining operations. It consists of a motor-driven propeller supported on a vertical shaft and submerged in the molten lead. The propeller is sometimes surrounded by a short cylinder or cone, open at the top and bottom, the upper rim of which is below the surface of the lead. The whole is supported on a frame bridging the kettle. The rotation of the propeller creates a vortex and a downward flow of lead at the center of the kettle. Any reagent to be mixed with the lead is drawn into this vortex, driven below the surface, and very thoroughly mixed with the metal.

Howard Dross Press.—The Howard press used for freeing dry drosses of mechanically entrained molten lead consists of a vertical frame supporting a vertical compressed-air or steam cylinder mounted above a shallow cylindrical receptacle, or

“basket,” with a drop bottom. The cylinder is fitted with a piston that may be raised and lowered, and the piston rod carries at its other end a plunger, or platen, that fits into the basket. In some designs the face of this plunger is provided with projecting prongs that penetrate the material being pressed and pass through holes in the bottom plate when the plunger is forced to the bottom of the basket.

In use the press is suspended over a kettle of molten lead having a layer of dross on its surface, the plunger is raised free of the basket, and the press is lowered until the rim of the basket is only a few inches above the surface of the lead. The dross is then skimmed from the surface of the lead into the basket until it is filled. The plunger is lowered and forced down under a pressure of 90 to 100 lb. per sq. in., compacting the dross and squeezing out a large part of the entrained molten lead, which escapes through holes in the bottom plate or around its edge.

To discharge the press, it is swung aside and the bottom plate is dropped, discharging the pressed dross in a cake on the floor.

Dross Basket.—A considerable amount of entrained lead may be removed from granular drosses by merely placing them in a perforated vessel and allowing the lead to drain. The vessel, or “basket,” usually takes the form of a 60-deg. steel cone 3 to 4 ft. in diameter and perforated with $\frac{3}{4}$ -in. holes. It is provided with a bail and a tail chain so that it may be tilted and dumped. The basket is suspended from a crane over a kettle of molten lead, and the dross is skimmed into it until it is filled. It is then lifted above the surface of the lead and allowed to hang and drain for a short time before being swung aside and dumped. The basket may be manipulated on the surface of the lead by the suspending crane in such a way as to skim the dross from the surface of the lead. The use of a vibrator on the dross basket, while suspended to drain, has been found to increase the removal of lead appreciably.

Removal of Bismuth.—Bismuth occurs with lead in most lead ores and follows the lead through smelting and refining operations, including desilverizing by the Parkes process, to the final refined lead. Commercial refined lead specifications set a maximum limit of 0.25 per cent bismuth in common lead. The presence of bismuth in lead within this range has practically no effect upon its properties for any application as a metal and is an advantage in that it improves the lead for certain alloys. When refined lead is used in applications where it is to be dissolved or corroded for producing chemical compounds, bismuth may be an undesirable impurity. This is particularly true in the production of basic carbonate white lead by the Dutch or the Carter process, where any impurity in the lead enters the white lead produced. Bismuth in such a case renders the white lead gray in color. For such uses “corroding lead,” containing less than 0.05 per cent bismuth, must be used.

Bismuth is removed from lead with other impurities at one operation in the Betts electrolytic refining process. The Pattinson process of desilverization removes bismuth to some extent with the silver; however, the removal is incomplete and the number of crystallizations and the amount of equipment required have made this process uneconomical for both silver and bismuth removal.

The Kroll-Betterton process for bismuth removal by the use of calcium and magnesium secures a very efficient removal of bismuth and is well adapted for application to desilverized lead as a step following the Parkes process.

Both calcium and magnesium will remove bismuth from lead when used alone, but when used in combination the efficiency of each is increased. These metals form compounds Ca_2Bi_2 and Mg_2Bi_2 which separate on cooling and can be removed as dross, similar to the zinc crust in the Parkes process.

Desilverized, dezinked lead, containing less than 0.01 per cent arsenic plus antimony, is treated with equal quantities of calcium and magnesium which are added at about 425°C. and thoroughly stirred into the lead. Magnesium is added as metal.

calcium is added as a 3 to 4 per cent calcium-lead alloy. The amounts of calcium and magnesium required to lower the bismuth to 0.02 per cent are indicated in Table 8.

TABLE 8.—KROLL-BETTERTON PROCESS

Bismuth in original metal, %	Reagent required, lb. per ton of lead	
	Calcium	Magnesium
0.10	1.30	1.30
0.50	2.15	2.15
0.80	2.90	2.90
1.00	3.40	3.40

The dross formed is removed by skimming and is recirculated in two stages similar to the Parkes process. The drossed lead contains 0.02 per cent bismuth and 0.05 per cent calcium and magnesium. The reagents are removed by chlorination or oxidation.¹

The dross is concentrated to about 50 per cent bismuth by liquation of lead and is then treated for production of refined bismuth.

Treatment of Zinc Crust.—Many methods have been tried for working up the zinc crust: distillation, smelting, cupellation, alkali-chloride fusion, steam oxidation, ammonium-carbonate leaching, but only one has survived—distillation of the zinc from the crust in a retorting furnace. This subject is treated more fully elsewhere in this volume.

Treatment of Intermediate Products.—Refineries tend to accumulate a large assortment of by-products that must be worked up into marketable products currently with the major operation. These intermediate products are described briefly below.

Softening Furnace Dross and Skimming.—The copper drosses from the softening furnace are usually not of great amount, since the lead bullion is usually freed from dross at the smelter. The drosses from the softener are ordinarily kept separate from the skimming. Where the dross is treated by itself, the procedure is a simple liquation in a small reverberatory. The furnace is charged and heated until the lead that liquates out of the dross forms a bath, on which the dry dross floats. When sufficient dry dross has accumulated, it is pulled out through the furnace door. The temperature is set low so that no dross is again melted into the lead. Dry dross recovered is smelted in the blast furnace; the lead goes to the softening furnace.

The treatment of antimony-softener skimming is an operation leading to the production of antimonial lead. This skimming is smelted in a reverberatory furnace with the addition of a high-grade galena or stibnite and fine coal. The metallic lead reduced from the skimming contains most of the precious metals. This lead, carrying about 1.5 to 4 per cent antimony, goes to the softening furnace. The matte produced, carrying copper, lead, antimony, and sulphur, is treated by concentration smelting. The liquated or refined skimming or slag, now carrying 15 to 20 per cent antimony, some arsenic and copper, and about 1 oz. of silver per ton, is usually removed as a liquid slag and goes to a blast furnace for producing hard lead, in which it is smelted with coke and metallic iron. In order to keep down the loss of antimony by volatilization, galena is sometimes added to the blast-furnace charge, its sulphur acting as a reducing agent. Only enough is added for this purpose so that no matte is formed.

¹ The use of magnesium and potassium together is covered by U. S. patent 2133327.

This addition of galena dilutes the antimony in the resulting hard lead. The antimonial lead ordinarily produced and marketed from this operation contains 15 to 18 per cent antimony. Antimony ore, either sulphide or oxide, may also be added to the blast-furnace charge. The hard lead finally obtained is usually drossed with

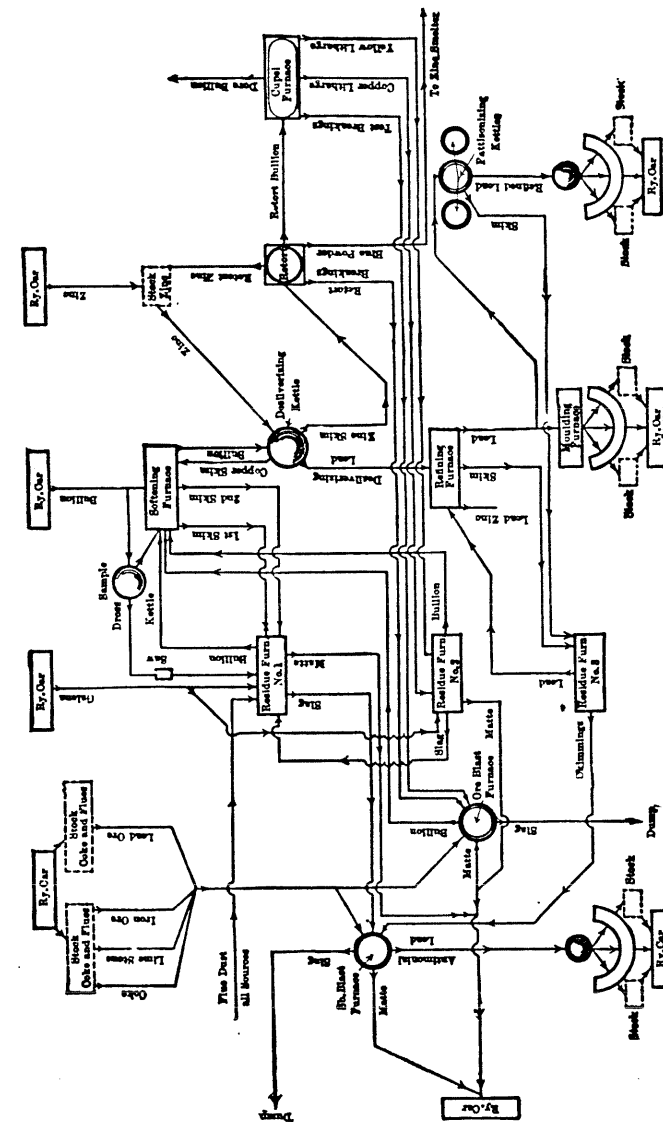


Fig. 66.—Flow sheet of lead smeltery and refinery.

sulphur in a kettle or liquated in a reverberatory furnace to remove copper that has been reduced in the blast-furnace operation. Some speiss is formed in the blast-furnace operation to remove arsenic contained in the reverberatory-furnace slag.

Kettle dross consists usually of lead oxide mixed with metallic lead; it is returned to the softening furnaces.

not been removed in the softening furnace, or by drossing, remains equally distributed between the liquid and crystal lead.

The process may be conducted in one of two standard systems, the method "by thirds," or the method "by eighths." In the first and more common method, two-thirds of the metal in the kettle is withdrawn in the form of crystals, one-third remaining as liquid metal richer in silver. In the second method, seven-eighths of the metal is taken out as crystals, one-eighth remaining as liquid. The distribution of silver in the crystals and liquid in the two methods is illustrated in the examples below, which are taken from practice, except that the assays are rounded figures.

Original Bullion—100 Tons—56 oz. per Ton—5600 oz. Total¹

"Thirds" Method	Weight, tons	Assay, Ag, oz. per ton	Total oz. Ag
Crystals.....	66.67	35	2,333.3
Liquid.....	33.33	100	3,333.3
Total.....	5,666.6

Original Bullion—100 Tons—20 oz. per Ton—2000 oz.

"Eighths" Method	Weight, tons	Assay, Ag, oz. per ton	Total oz. Ag.
Crystals.....	87.5	14	1,225.0
Liquid.....	12.5	60	750.0
Total.....	1,975.0

¹ Figures are from private notes of H. S. Levison, Am. Smelting & Refining Co.

The method by eighths was applicable only to bullions low in silver. With rich bullion the proportion of silver retained in the crystals became prohibitively high, and the method by thirds was more economical.

The original hand-labor Pattinson process was, until recently, in use in England and Germany. Machinery has been introduced to reduce the labor of withdrawing crystals and ladling out the liquid lead, the two principal mechanical modifications of the original process being the Luce-Rozan and the Tredinnick. In both, the metal is stirred by steam and the liquid drawn off, leaving the crystals in the kettle.

The procedure of the original process, using the method by thirds, is as follows: The kettles, varying in number from 8 to 15 according to the richness of the bullion, are arranged in a row, the position of the charging pot, or kettle in which the work lead is first melted down, varying in accordance with the proportion of silver in the lead. The pots are numbered in series, from the market lead end upward; the charging pot may be, in a series of 12 pots, anywhere between No. 6 and No. 10.

The melted bullion in the charging pot is poled and drossed, and the fire withdrawn and transferred to the next pot, in the melting stage. Crusts forming at the sides of the pot are pushed down into the lead to be remelted, and the bath is continuously stirred in order to ensure uniform cooling throughout. As crystals form, they are lifted, drained, and transferred, when dry, into a neighboring pot, usually "down the house," to the right. This continues until two-thirds of the contents of the charging pot has been removed, when the remaining one-third of still liquid lead is ladled into the adjoining pot, "up the house," to the left. If there is then on hand, from previous operations, lead equal in silver contents with that in these two right and left pots, respectively, an exactly similar operation is commenced with each of these simul-

taneously. The charging pot thus becomes filled from the crystals of the kettle at its left and the liquid lead of the kettle at its right. In this same manner the operations are continued, the kettles "down the house" decreasing in silver tenor and the kettles "up the house" increasing, until the silver content of the lead in the market kettle at the extreme right is 0.3 to 0.5 oz. per ton, and that of the liquid lead at the extreme left is at the maximum, about 500 oz. Before the whole plant can be in working order, a number of crystallizations must be performed in order to have on hand the necessary amounts of lead of different silver contents required to fill the several kettles.

The Luce-Rozan Method.—In this modification of the Pattinson process, steam is used for stirring, and the apparatus and the arrangement of plant are of radically

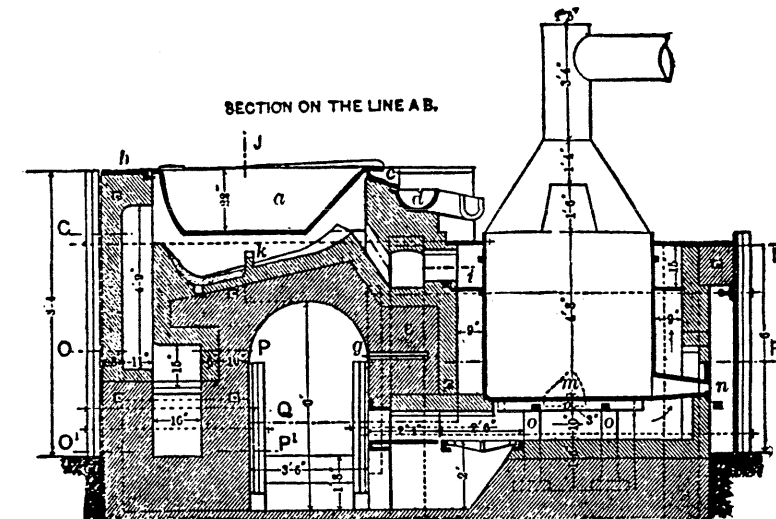


FIG. 68.—Luce-Rozan plant.

different nature. The plant is shown in Figs. 68, 69, and 70, and consist of two melting pans *a*, one crystallizing kettle *b* (Fig. 70), and two large conical molds, instead of the long line of some 12 kettles of the original Pattinson arrangement. The two cast-iron melting pans, used alternately, each holding 7 tons of lead, can be raised by means of a steam crane, so as to pour their contents into the crystallizer, which holds 20 tons.

The mode of working is as follows: The bullion is melted down in one of the melting pans, drossed, and run into the previously heated crystallizing kettles by raising the back end of the pan. In the crystallizer it is stirred by steam at 45-lb. pressure, cooled by withdrawal of fire and by water sprays, and two-thirds of the contents become crystallized. The still liquid lead is then run into the conical molds from the crystallizer, and the fire under the latter replaced and the crystals (13½ tons) remelted. In the meantime, 6½ tons more of lead, with the same silver content as that in the crystallizer, has been melted down in one of the pans, so that, as soon as the crystals have been remelted, it can be run in and a new operation begun. The other melting pan contains lead equal in silver content to the crystals that it is expected will be produced from the next operation, and this second pan is being melted down in readiness for the next following crystallization.

Eleven crystallizations are necessary to obtain market lead from lead bullion averaging 146 oz. of silver per ton. Six charges are run in 24 hr. Two men per shift attend to the crystallization; all lead handling is done by a crane man and helper. As in the hand Pattinson process, a number of preliminary crystallizations—66 at Pribram, Czechoslovakia—must take place to furnish the necessary intermediary grades of lead for normal work.

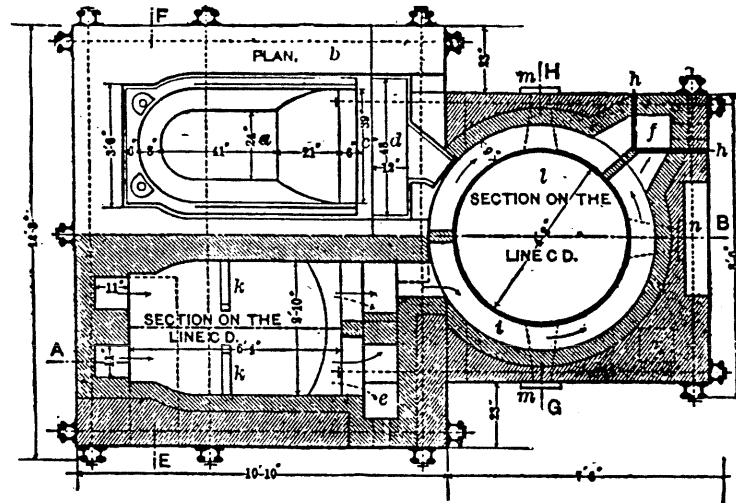


FIG. 69.—Luce-Rozan plant.

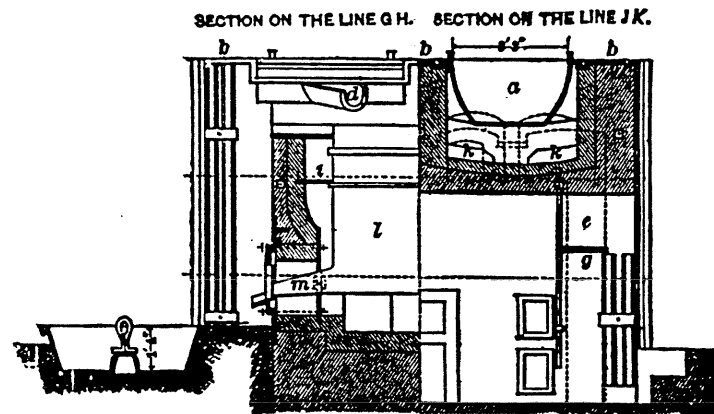


FIG. 70.—Luce-Rozan plant.

Products of the process (from above bullion) are rich lead of about 262 oz. of silver per ton, desilverized lead of about 0.43 oz. per ton, dross, and flue dust. The rich lead is cupelled, the desilverized lead is refined in a reverberatory furnace to remove arsenic and antimony and then molded into market bars, and the dross and dust are worked up with similar by-products from other parts of the works. A curious by-product sometimes encountered in the steam Pattinson process is a small incrustation of minium—red lead—which forms in the crystallizer, produced by the action of steam on the lead at a temperature just below redness.

The Luce-Rozan method runs into greater plant cost and maintenance than the original Pattinson, but its advantages more than offset these items. Softening of the lead bullion is not so imperative; the cost of labor is only 30 per cent, and of fuel 40 per cent, of the Pattinson cost; and only about one-third of the amount of drosses obtained in the Pattinson cycle is produced in the Luce-Rozan.

Other Pattinson Processes.—Several other variations of the Pattinson process have been developed and used to some extent. These do not introduce any new principles but differ in the equipment used and reduce the time required for the process very materially. These include the Tredinnick process and the Hall process. The Pattinson process is not used in the United States for desilverizing at the present time.

Cupellation.—The rich leads from the Pattinson process, containing 250 to 600 oz. of silver per ton, and the retort bullion from the Parkes process, containing 2000 to 5000 oz., are finally treated by cupellation for the separation of the precious metals. This process consists essentially of melting the rich lead in a reverberatory furnace and exposing it to a blast of air, by which the lead and the base metals are oxidized and slagged off in the form of litharge of varying degrees of purity, while the silver and gold, having scarcely any affinity for oxygen, remain behind in metallic state. The oxidation is accomplished mainly by the action of the air blast and partly by the action of the molten litharge, which absorbs an excess of oxygen and gives it off to the underlying impurities Cu, As, Te, and Se. The cupellation of gold-silver-lead and the parting of doré bullion are discussed elsewhere in this volume.

CHAPTER VIII

TREATMENT OF ZINC CRUST AND ELECTROLYTIC SLIME
PART I. TREATMENT OF ZINC CRUST PRODUCED FROM
DESILVERIZATION OF LEAD BULLIONBY T. D. JONES¹

Introduction.—In this section the treatment of zinc crusts produced in the Parkes desilverizing process will be described. In the process of desilverizing, the refineries, if conditions warrant, can carry out a separate degolding operation, the crust being treated separately from the silver-zinc crust. However, in general, it is regular practice to remove the gold and silver in the regular desilverizing crust, paying particular attention to crust enrichment, so that at the present time so-called silver-zinc crust will assay 3000 to 8000 oz. doré per ton and 30 per cent zinc. The crust is then subjected to the distillation or retorting process for the recovery of zinc, which is returned to the desilverizing process.

Retorting.—The Faber du Faur type retort furnace is universally used for retorting. In former times the furnace was cubical in shape. However, many improvements have been made in construction so that at the present time the outside dimensions of the furnace are generally 3 ft. 10 in. in width and 4 ft. in depth, the over-all length being 6 ft. The furnaces are well-balanced tilting furnaces equipped with a suitable cast-iron shell which swings on trunnions. Modern furnaces are well insulated, the cast-iron shell being lined with suitable insulating material, the inner lining being of 9-in. fire-clay or high-alumina brick.

The arch of the furnace is so constructed that it follows closely the contour of the retort crucible in place. Every effort has been exercised in the firebox construction to provide conditions that would produce the maximum temperature adjacent to the retort crucible walls.

Retort furnaces are generally heated by gas or oil and are fired from the front or rear of the retort. While considerable controversy has existed over proper firing arrangements, experience has shown that the position of the burners has relatively no effect on the actual results obtained. The flue opening from the firing chamber is always on the same side as the burner, and this provides for sweeping action of the hot gases in order to obtain maximum fuel efficiency.

Formerly, the retort-furnace flues discharged into a large main brick flue and thence to a stack. Most recent installations provide for individual stacks of steel construction into which excess cold air may be drawn for cooling purposes. Usually, three individual stacks lead to a common header pipe, extending through the roof. This type of construction provides ample working space and excellent working conditions for the operators. Today, with modern construction and ventilation, retorting becomes a very desirable operating job, whereas, in former times, it was most unattractive to the operators.

The retort crucible, or No. 11 crucible, as termed by the manufacturer, is of standard shape and produced from select clays and Madagascar large-flake graphite.

¹ Traveling metallurgist, American Smelting & Refining Co.

Great progress has been made in details of retort construction, which, together with proper preheating facilities by the refineries, has increased retort life from 40 charges 10 years ago to 70 charges at the present time.

It is general practice to store retorts in hot drying chambers at the refineries and remove directly from the hot chambers to the retort stands as required. When setting the retort crucible, it is always good practice to provide a new stool or pillar, as a defective stool will cause the retort to shift during operation and breakage will result. The crucibles are usually set on the stools at an angle of inclination of 30 deg. from the horizontal. In this position, the crucible will have a capacity of 1300 to 1400 lb. of sized Parkes silver-zinc crust and also provide maximum heating area. The neck of the bottle is supported by brickwork, the top of the neck extending out 1½ in. from the face of the brickwork.

Considerable care must be used in starting retorts under fire. It is good practice to raise the temperature slowly, allowing approximately 8 hr. to reach maximum temperature. During this period, charcoal or other reducer must be placed inside the retort, in order to prevent excessive oxidation of the retort lining. It has been determined that the clay mix does not glaze over until a temperature of 1700°F. is reached, and unless a reducing agent is present during the heating-up period considerable life may be lost.

Condensers are usually of cast-iron construction, supported by a condenser stand. Modern construction provides for the condenser stand to be fastened to the furnace trunnion, and the stand swings in an arc and is held in place by a toggle hook. Suitable high-velocity ventilators extend over the mouth of the retort, in order to remove any escaping fume.

Once the retort has been charged and the condenser is in place, the minimum amount of fire clay or adobe for luting is used. Excessive use of adobe or fire clay causes the condenser to burn out.

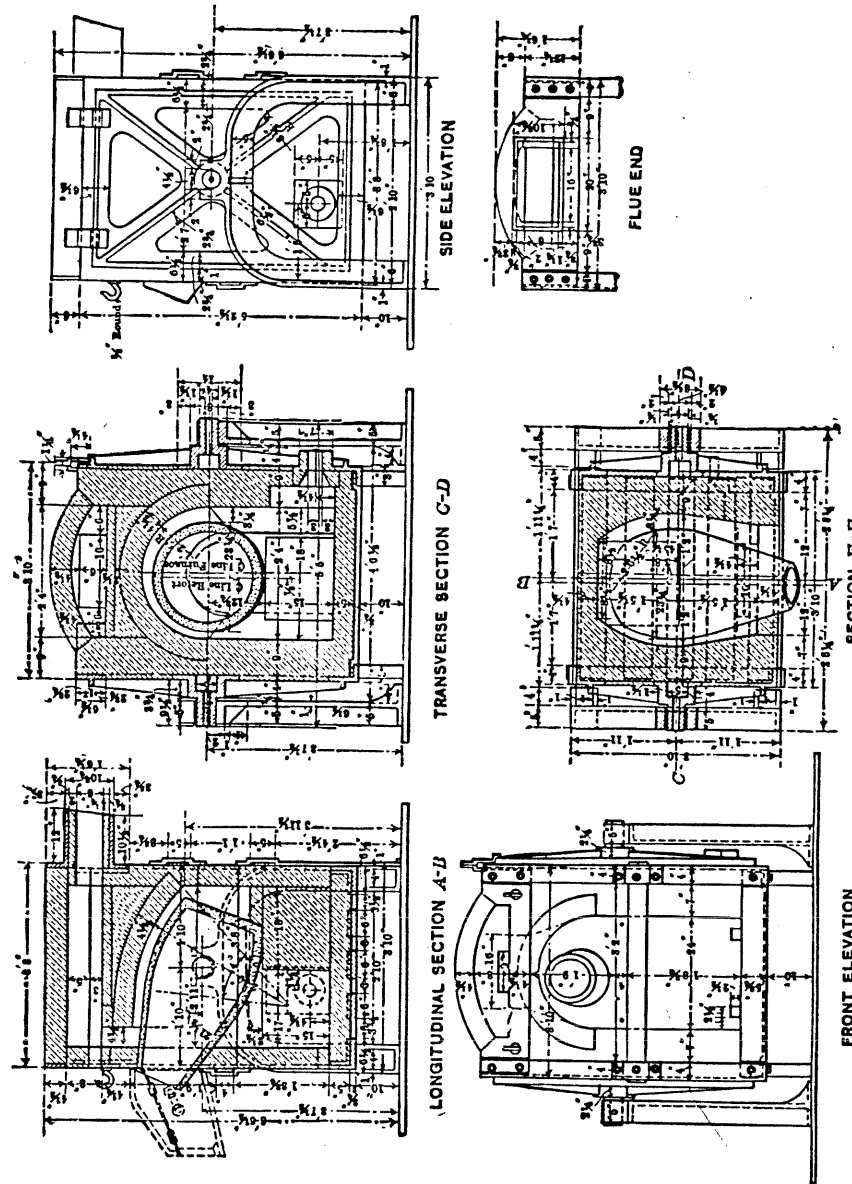
The proper operating temperature for retorting is approximately 1260°C., or 2300°F. Distillation requires 6 to 8 hr., and during this period approximately 420 lb. of zinc is distilled and cast into 50-lb. slab bars. Blue powder, approximately 12 lb. per charge, is formed during the operation, and the blue powder can largely be controlled by producing high-grade silver-zinc crust. Inferior silver-zinc crust containing much fine material requires a longer time for distillation, with subsequent increase in production of blue powder. The production of blue powder can be greatly reduced by adding flux with the silver-zinc crust charge. Still another practice to reduce the net blue powder produced is to screen the production, using totally enclosed shaker screens and returning the metallics directly to the retort charge, the end product, relatively low in doré, being shipped to a zinc smelter for recovery of zinc.

During distillation the condenser is of a cherry red color, and toward the end of distillation this color disappears and the condenser becomes dark in color, which indicates that the charge is nearly cooked.

The fuel oil required per ton of silver-zinc skim ranges from 40 to 60 gal., and where gas is used, the equivalent amount of B.t.u. is required. One man will operate three retorts per shift and at times can handle four retorts. The zinc in the final retort metal will analyze 1½ to 2½ per cent zinc. The retort metal assays 6000 to 14,000 oz. doré per ton, depending on pretreatment of silver-zinc crust prior to retorting.

Cupellation of Retort Bullion.—Considerable improvement has been made in cupel-furnace construction. While the old conventional type, comprising a removable test pan and stationary side walls and arch, is still in use, modern cupel construction consists of a sheet-steel shell resting on a tilting mechanism. The hearth, side walls, and arch are contained in the steel shell and are a complete unit.

While the old type test pan made from crushed limestone and fire clay usually had a life of 30 to 50 days, the new type cupels, having a high-alumina brick bottom, magnesite or high-alumina brick side walls up to the metal line, the upper side walls



Figs. 1-6.—Oil-fired zinc-crust furnace.

and arch of fire-clay brick, will have a life of 6 months. The magnesite or high-alumina side walls and bottom will last 8 months with the aid of patching material, which is common operating practice.

Cupels in general are usually heated by oil or gas, the burners being located in the rear of the furnace directly opposite the charge door.

The new type cupels have a novel flue arrangement, the off-take flue being constructed of heavy sheet steel, built in sections which are adjustable. The off-take flue rests in position just over the charge door to the cupel, and sufficient extraneous air is drawn in with the hot cupel gases and fume to provide cooling, permitting the use of sheet-steel flues that have many advantages over the old-type brick flues.

The cupels are fitted with water-cooled jackets that serve to hold the breast of the cupel. The only reason for using water is to protect the breast material that is cut down by the operator during the cupeling cycle. A cupel is equipped with two or more tuyères, extending into the furnace through separate ports on either side of the burner ports. Compressed air at a pressure of 16 to 20 oz. is admitted through the tuyères in order to obtain rippling action on the surface of the bath. To obtain proper cupeling conditions, the tuyères are adjustable so that the air stream may be directed in any desired manner.

Cupels vary in size according to the doré output of the respective refineries. At the present time, cupels are capable of producing 100,000 to 350,000 oz. of finished doré per charge, the latter having outside dimensions of 7 ft. 11 in. in width and 10 ft. 2 in. in length, with a bath depth of 14 in. Where the larger cupels can be used, there is a considerable advantage, as the doré output per day, per cupel, is greatly increased, thus resulting in lower costs.

Under normal operating conditions, cupels are charged by adding cold bullion bars or hot charged from ladles containing hot retort bullion from the retorts. Bars or hot charges are added intermittently during the cupellation period until sufficient doré is present for a full doré charge.

The impurities found in retort metal are, as a rule, zinc, arsenic, antimony, copper, bismuth, and tellurium—a typical analysis being as follows:

DORÉ—6000 TO 14,000 OZ. PER TON

Impurity	Per cent	Impurity	Per cent
Zinc.....	1.5-2.5	Tellurium.....	0.2
Arsenic.....	0.4	Bismuth.....	0.25
Antimony.....	1.0	Lead.....	Balance
Copper.....	1.5-4.0		

The process of cupellation has for its object the separation of silver and gold from lead and the above-mentioned impurities. The operation of a cupel consists of first filling a cupel approximately one-half full of retort metal, melting down, and approaching a temperature of 2100°F. The tuyères are opened, and the bath is thoroughly rabled in order to incorporate the zinky retort dross with the litharge formed during the early stages of cupellation. The thought is thoroughly to demetallize and desilverize the heavy drossy material which is relatively high in zinc.

The impurity zinc is readily oxidized, about 25 per cent going to the baghouse and 75 per cent collecting in the litharge. As soon as the cover slag thins down to the point where it can be removed from the cupel, the furnace is tilted and the zinky litharge drawn off through the breast to suitable portable pots or pans. As a cupel cycle may consume as much as 3 days, it is understood that current production of retort metal is continuously added to the cupel bath or until such time as there is sufficient doré present for a full charge. During this charging period, litharge containing most of the zinc and a portion of the copper has been withdrawn from the

furnace, in order to make room for additional doré material. During this period, the arsenic and antimony content have also been removed, the greater portion being contained in the litharge.

The final stage of refining consists in removing lead, copper, bismuth, and tellurium. The copper is removed gradually, being continuously oxidized by the large amount of PbO that is present. During the latter stages of refining, the litharge is properly termed copper litharge as it may contain as much as 10 per cent copper, while so-called good litharge will contain approximately 1 to 1.5 per cent copper. Bismuth concentrates in the doré until the last stages of refining, when it becomes oxidized and is removed with the litharge. After the last litharge is removed, it is often necessary to add approximately five bars of refined lead to form additional litharge, in order to remove the last traces of impurities with the exception of tellurium. Tellurium tends to remain with the silver and is removed by successive treatments with sodium nitrate after all the litharge is removed. Fully refined doré will assay 995 parts per thousand gold plus silver, the balance being largely copper. The doré is cast into anodes for the electrolytic parting process or plates for the sulphuric acid refining process.

In instances where the doré is shipped to distant parting plants, it is cast into bars, using molds similar to those used for refined silver bars.

One man per shift is required for the operation of each cupel, and the fuel varies directly with the size of the cupel. The large cupels, having a capacity of 300,000 oz. doré, will require 270 gal. of oil per day, the cycle on the larger cupels being 3½ days.

PART II. TREATMENT OF ELECTROLYTIC SLIMES

BY DONALD M. LIDDELL¹

Treatment of Copper Slime.—The slime produced in the electrolytic refining of copper varies in both quantity and composition with the kind and grade of anode metal refined. Most of the refineries attempt to blend and refine the pig copper in the anode-casting furnaces in order to secure anode metal assaying about 99 per cent copper. The yield of slime from this grade of anode metal should average between 1 and 2 per cent of the weight of anode dissolved. Typical examples of copper anode slime are given in the following table:

	1	2	3	4	5	6	7
Ag, ounces per ton.....	6220.4	4680.5	14,012.8	9631.5	3600.0	927.90	310.5
Au, ounces per ton.....	143.6	64.5	91.7	96.55	800.0	402.75	10.15
Cu, per cent.....	18.24	28.09	13.53	4.47	40.0	69.03	46.53
Ni, per cent.....	1.63	2.64	0.54	0.27	2.03	23.13
As, per cent.....	0.32	1.12	2.16	1.97	0.15	0.28
Sb, per cent.....	4.56	3.54	3.04	7.20	0.15	0.68
Bi, per cent.....	Trace	None	Trace
Se, per cent.....	18.05	16.14	4.27	1.15	22.0	0.85	6.60
Te, per cent.....	2.36	2.21	1.07	0.85	3.7	1.50	0.27
Pb, per cent.....	4.95	1.93	8.83	25.34	0.79	1.53
Zn, per cent.....	Trace	Trace
S, per cent.....	3.31	4.09	5.31	4.99	15.41	1.58
Fe, per cent.....	0.41	0.53	0.38	0.25	1.04	0.41
SiO ₂ , per cent.....	4.27	6.35	0.43	0.41	0.93
Sn, per cent.....	1.05	0.23	0.15	0.09	0.31

¹ This section is a major revision of the contribution by W. C. Smith in the original edition.

Samples 1 to 4 were composite samples of the slime from at least 10,000 tons of anodes. Sample 5 is in the main a slime derived from Noranda bullion. Sample 6 was taken from a run made on low-silver, high-gold anodes; sample 7 was taken from a run on high-nickel anodes.

Slimes-treatment processes,¹ to be successful, must fulfil several requirements which may be listed as follows: minimum metal loss; prompt delivery of the bulk of the gold and silver; delivery of the by-products in a recoverable form; economy of operation; and the introduction of no chemicals to the process which may have an injurious effect on the refining of copper if they later enter the electrolytic circuit.

In the early days of electrolytic refining, the slime was screened to remove metallic copper, washed to free it of soluble copper salts, filtered to remove excess water, and cupeled with lead in a cupel furnace. The lead loss was heavy, and the litharge was fouled with copper. It was discovered that much better results were obtained in the furnace work with a slime from which the copper had been removed.

Copper Removal.—The first method employed for the removal of the copper from screened raw slime was to boil the slime with dilute sulphuric acid to which sodium nitrate was added in small doses. The boiling operations were conducted in lead-lined tanks equipped with paddle or air agitators; the slime was run into the tank, and enough sulphuric acid was added to make a 50 per cent sulphuric acid solution; the mixture was then heated with steam to the boiling point, and the sodium nitrate was added a few pounds at a time. Heavy fumes of poisonous nitrous gases were given off, and if the sodium nitrate was added in too large doses, the charge would foam over the top of the boiling tank. It often required 48 to 72 hr. to reduce the copper in the treated slime to 2 to 3 per cent. The lead tank lining was rapidly attacked and needed frequent repairs. The copper solution from the slime leaching was settled to remove the last traces of suspended slime and added to the tank-house electrolyte. So long as the electrolyte purification system withdrew a large volume of solution for the manufacture of copper sulphate, no trouble from sodium compounds in the electrolyte was experienced, but with the decreased market for copper sulphate and the cyclic purification methods later developed for electrolyte treatment, the sodium salts accumulated in the electrolyte and caused trouble.

The raw slime was also treated for the removal of copper by boiling with 50 per cent sulphuric acid to which manganese dioxide was added in small quantities at a time, until the copper had been oxidized and dissolved. The addition of an excessive amount of the manganese dioxide at one time would cause the charge to foam over the top of the boiling tank. The copper solution from the boiling of the slime contained manganese sulphate, and this solution could not be added to the regular electrolyte as the manganese salt caused trouble in the electrolytic cells. The solution was, therefore, sent to the copper-sulphate plant and was used for the production of blue-stone. The manganese salts eventually went to waste in the spent liquors from the iron cementation tanks in which the last of the copper was precipitated from the mother liquors. These methods have been superseded by one of the several forms of either oxidizing roast or sulphatizing roast, followed by leaching with dilute sulphuric acid or water.

Oxidizing Roast.—When screened raw slime is subjected to an oxidizing roast, most of the copper is rendered soluble in dilute sulphuric acid.² This is due to the conversion of the copper and cuprous oxide into cupric oxide. The greater part of the copper in some slimes is rendered soluble at as low a temperature as 140°C. However, a temperature of 400 to 500°C. is required with most of them to render 95 per

¹ ADDICKS, "Copper Refining," p. 107.

² However, it seems preferable to use the sulphatizing roast rather than a plain oxidation, as this also eliminates much of the selenium.

cent of the copper soluble. Roasting at the higher temperatures usually also renders some of the silver and selenium acid-soluble. The details of roasting experiments on slimes 6 and 7 of the table on page 220 are as follows:

Sample	Roast, 6 hr. at, °C.	Per cent acid-soluble Cu		Soluble Ag	Soluble Se
Slime 6	140	12.34		No	No
	250	71.96		No	No
	400	91.96		No	No
	500	96.53		Yes	No
Slime 7	200	31.16	6.73 Ni	No	No
	300	67.90	10.57 Ni	No	No
	400	91.58	38.62 Ni	Yes	No
	550	99.30	11.53 Ni	Yes	Yes

Sulphatizing Roast.—Over 30 years ago, Dr. Edward Keller found that if slimes were roasted with sulphuric acid practically all the copper was converted to copper sulphate. It was his opinion that if stoichiometric proportions of acid were employed for combination with the copper optimum results were obtained. It appears, however, to be the opinion today that the best results follow with the acid in excess.

Probably the treatment of slime at Ontario East as given by C. W. Clark and A. W. Heimrod¹ and C. W. Clark and J. H. Schloen² represents the most modern practice that has been described.

The original slime carries 40 per cent Cu, 3600 oz. Ag per ton, 800 oz. Au per ton, 22 per cent Se, and 3.7 per cent Te. These slimes after filtering are dried at 250 to 300°F. to about 10 per cent H₂O. At this moisture there is very little dusting. They are then mixed with 75 per cent of 60° sulphuric acid and roasted at 700 to 800°F. in a Herreshoff furnace. Acid is also sprayed into the roaster during this process so that a total acid consumption of 2.2 to 2.5 lb. of acid is used for each pound of copper present.

Over 95 per cent of the copper is rendered soluble by this means, and the use of this excess of acid causes the volatilization of 80 to 95 per cent of the selenium present which is caught in the fume-collecting system attached to the roasting furnace. The collected fume furnishes the basis for the plant's selenium recovery. The slime after leaching with the copper carries about 4 per cent Cu, 11,700 oz. Ag per ton, 26 oz. Au per ton, 15 per cent Se, 11 per cent Te. If the copper-sulphate solution shows silver, it is precipitated with a little copper scale. The solution after removal of silver is electrolyzed to produce copper and sulphuric acid, the acid being used in the treatment of future slime.

After removal of the copper, the slimes are leached with caustic-soda solution which removes the tellurium by washing, as sodium tellurite, which is used as a source of tellurium. The filtered and washed slimes contain about 4 per cent Cu; 12,000 oz. Ag per ton, 2700 oz. Au per ton, 14 per cent Se, 1.5 per cent Te.

These slimes are smelted with soda and fine silica in a doré reverberatory furnace with magnesite lining. The first slag contains most of the lead, arsenic, antimony, and iron and goes back to the anode furnace. The charge is then blown with air with fused soda ash for flux to eliminate the tellurium. This second slag is leached with the caustic liquor from the slimes treatment, which takes out the selenium and tellurium, the leached slag going to the anode furnace.

¹ *Trans. Electrochem. Soc.*, Vol. 61, 1932.

² *A.I.M.E., Tech. Paper* 982, Class D 57, 1938.

The doré in the furnace is given a final refining with niter to remove the copper, this slag going back also to the anode furnace.

Furnace Refining of the Treated Slime.—The first refineries treated the boiled and leached slime with lead in cupel furnaces, and this method is used today at those plants which refine both lead and copper. One method for charging the slime to the cupel furnace consisted in packing the slime in small paper bags which held 15 to 25 lb. of slime and in charging the bags of slime onto the surface of the molten lead in the furnace. This method probably caused a heavy dusting loss. A better method consists in mixing the slime with litharge and a little fine coal and smelting the mixture in a small basic-lined reverberatory furnace to a slag and metal. The metal is cast in the form of bars and is fed to the cupel as needed; the slag is smelted in the lead blast furnace. Most of the copper refineries are not operated in conjunction with a lead refinery; hence other methods of treatment were developed.

The melting of treated slime in a basic-lined reverberatory furnace yields a lead-antimony slag, called tapped or sharp slag, and a metal that consists of Ag, Au, Se, Te, some Cu, and other metals. If the slime carries considerable selenium or tellurium, a third product, a matte or speiss, in which selenium and tellurium take the place of sulphur, may be formed. This matte or speiss is a most troublesome material to handle and may carry as much as 50 per cent silver. Several methods are used either to prevent the formation of this matte, or to decompose it after it has been formed.

Fluxing the Slime.—The treated slime is often mixed with fluxes before charging to the melting furnace. The fluxes used are silica, lime, soda ash, salt cake, niter cake, caustic soda, or a mixture of several of these. The thin slag that is formed is tapped from the furnace, and the metal is oxidized by forcing compressed air under the surface of the metal through iron pipes. A second slag is formed, which is skimmed off, and the metal is refined to doré with air and niter, or niter and soda ash. When slimes carrying excessive amounts of copper, selenium, and tellurium are being furnace, a matte will separate from the metal during the refining process; this matte retards the refining operations and is best handled by tapping off, crushing to 10 mesh, roasting and leaching with sulphuric acid for the removal of the copper before returning to the melting furnace.

The following data¹ show the composition of the matte at different stages during an attempt to oxidize it in the melting furnace by means of air, niter, and soda ash. Samples were taken every 4 hr. over a period of 28 hr.

Sample No.	Au, ounces per ton	Ag, ounces per ton	Cu, per cent	Se, per cent	Te, per cent
1	139.15	13,751.8	20.67	22.83	0.50
2	105.55	14,336.0	22.88	20.80	1.20
3	67.42	14,139.3	25.33	19.34	1.35
4	25.70	12,016.0	33.07	15.25	1.52
5	18.15	9,685.1	33.81	12.05	2.48
6	10.20	8,707.9	31.83	7.67	2.44
7	6.85	8,102.5	47.32	0.62	1.20
8	5.10	7,664.9	49.40	0.15	0.07

¹ Personal notes of W. C. Smith.

These slimes had been given an oxidizing roast only, and the difficulty of eliminating the selenium shows the advisability of the sulphatizing roast.

At one plant, the treated slime is melted without flux to a sharp slag and a matte or speiss and metal in one furnace; the slag is tapped off, and the metal and speiss are transferred to a second furnace in which the mixture is refined to doré with air, caustic soda, and niter.

The sharp slag from the slime-melting furnace usually carries 0.5 to 4 oz. per ton of gold; 125 to 500 oz. per ton of silver; with varying amounts of copper, lead, and antimony. A typical slag will assay about as follows:

Oz. per ton		Per cent							
Au	Ag	Cu	Pb	Ni	As	Sb	Se	Te	SiO ₂
0.80	458	3.99	16.76	0.27	0.97	5.18	0.58	0.52	18.0

The sharp slag is sold to the lead smelter for the gold, silver, and lead contained in it; is smelted to copper matte in the ore-smelting furnaces and the matte blown to blister copper in converters; charged to the anode furnaces; or smelted to black copper in the copper blast furnace. The last two methods are the least desirable, since the sharp slag contains many impurities which go into the anode or the black copper and are circulated through the process. A partial elimination of these impurities is made in both the matte smelting and converting operations; hence this method of treatment gives a better elimination of the impurities, but, unfortunately, many of the refineries do not smelt sulphide ores.

Sharp slags, which contain high silver values, and the second slags, produced during the refining stage, are generally re-treated in the slime-melting furnaces either with slime or in separate campaigns, and eventually report as sharp slag.

The soda-niter slags are either charged to the slime-melting furnaces with slime, or are first crushed and leached for the removal of the selenium and tellurium contained in the slime, and the leached residue is returned to the slime furnace.

Slime Furnaces.—Small oil-fired reverberatory furnaces lined with magnesite or chrome brick are used for the melting of the slime. The charge is introduced at intervals, and each batch is melted down before the next charge is made. Sharp slag is often tapped from the furnace several times before the furnace is fully charged. It is customary to add a small amount of coal to the slag, $\frac{1}{2}$ to 1 hr. before the slag is tapped, in order to secure a cleaner slag. The slime may be charged to the furnace through the regular working door by shoveling, or by dropping from hoppers through charge holes in the furnace roof. The life of a furnace bottom is 6 to 12 months; the side walls and roof require patching about every 30 to 60 days.

Metal absorption of a furnace is almost directly proportional to the volume of the brickwork below the metal line of the furnace; hence, in order to reduce the interest on the metals tied up in furnace linings, the furnace should be of such design as to have the maximum capacity with the minimum of lining consistent with good fuel consumption and furnace life. A thinly lined cylindrical tilting furnace has been developed. Two small furnaces of this construction replaced one furnace of the stationary type; each furnace melts and refines a charge of 6 to 8 tons of slime in 48 to 60 hr., while the larger furnace requires 90 to 120 hr. to treat 12 to 15 tons of slime. The two small furnaces absorb less metal than the single larger furnace and also make

an interest saving of 5 to 6 days on the metals in process. This saving is made by the reduced time the slime is waiting for furnace treatment, the reduced time the metal is in the furnace, and the reduced time the doré is awaiting parting because of the delivery of very large batches to the parting plant necessary with the large furnace.

Metal Losses.—The gases from the slime-roasting, -melting, and -refining furnaces contain Ag, Au, As, Sb, Se, and Te; hence some method for the recovery of the values from the furnace gases is necessary. The losses are due to both volatilization and mechanical dusting of the charge. As much as 1.25 per cent of the silver in the slime treated has been recovered from the furnace gases. The earlier plants used settling chambers and water scrubbers, but these were never satisfactory. Baghouses could not be used because the acid in the gases rapidly destroyed the bags. Cottrell precipitators are used for this work with good results. The treaters may handle the gases either hot, or wet and cold. The hot treater can be made of steel, but the wet treater must be constructed of lead or other acidproof material. The wet treaters are more expensive to build than the hot treaters, but have found the most favor.

There seems to be no question that silver refineries should be equipped with both scrubbers and Cottrell precipitators. The very modern plant at Ontario East has a brick flue followed by a steel flue in which the gases cool to about 400°F. and from which they enter three tower scrubbers that are fitted with sprays and rain plates. About 90 per cent of the material that passes the flues is recovered in these scrubbers. The gases leave the scrubbers at about 125°F. and go to Cottrell tube precipitators 12 ft. long. A constant watch is kept on the effluent gases from the Cottrell, but the loss is said to be less than \$2 a day. Both the scrubber system and the Cottrell use antimonial lead to resist the highly corrosive gases. The scrubber solution goes to the selenium precipitating plant, while the scrubber mud goes back to the slimes-roasting furnace.

Recovery of By-products.—The by-products of greatest commercial importance in copper slime are selenium, platinum, and palladium. The platinum and palladium remain with the gold and silver, are delivered to the parting plant in the doré, and are recovered during the refining of the gold. Reference should be made to the separate chapters covering these metals.

Wet Methods for Slime Treatment.—Much thought and money have been expended in trying to develop wet methods for the treatment of slime, and several promising schemes have been given large-scale tests, but no such methods are in use at the present time. The wet treatment of the slime for the removal of the copper, followed by furnace refining to doré and the parting of the doré, is far from perfect, but yields better results than any wet process known. The methods used for the treatment of the lead slime produced by the Betts process of lead refining are given on page 378, Electrolytic Refining of Lead, and pages 141 to 142, Bismuth.

Treatment of Electrolytic Tin Slime.—The American Smelting & Refining Co., at the Perth Amboy, N. J., plant, at one time operated an electrolytic tin refinery. Very little information relative to the process has been given out. It is known that the impure tin treated carries lead, bismuth, and silver as the chief impurities. The slime is said to have carried Sn, 30; Pb, 20; Bi, 20; Cu, 5; As, 3; Sb, 5; and it is said over half the lead was present as sulphate. No details of its treatment were given out, nor has the author ever been able to ascertain the precious-metal content. If the slime were to be charged to the cupel furnaces the tin would be lost.

OTHER SILVER- AND GOLD-BEARING MATERIALS

Treatment of Cyanide Bullion.—The silver bullion produced by the cyanide treatment of silver and silver-gold ores is often refined and parted at the large refineries

Precious
Metal
Gases
Recovery

on a custom basis. The bullion is weighed and sampled, either by drill sampling or by melting and dip sampling, charged to the cupel furnaces or the slime-refining furnaces, and refined to a suitable doré for parting.

The cyanide precipitates at Pachuca, Mexico, are first treated with dilute sulphuric acid to remove as much zinc as possible; are then melted in a basic-lined reverberatory furnace; and are refined with air to a very high-grade doré for electrolytic parting. Low-grade cyanide precipitates are treated at some of the lead refineries by mixing with litharge and a small percentage of coal, and smelting to a rich lead, which is then treated in the cupel furnaces.

Sulphide precipitates are handled in the same manner, except that no coal is used in the mixture; the sulphur in the precipitates reduces sufficient litharge to metallic lead to collect the values. The litharge slags from this furnace are re-treated in the lead blast furnace.

Jewelry Sweeps and Other Industrial Wastes.—These materials are usually in a very finely divided state when received, and are sampled and graded into two classes according to the assay value. High-grade material is often charged directly to the cupel or slime furnace in order to get the bulk of the precious metals on the market as soon as possible. The low-grade materials are sintered, briquetted, or nodulized with other fine material and smelted in either lead or copper blast furnaces. The lead bullion or copper matte, or both, serve as the collector for the precious metals, and these products are treated for the precious metals they contain. The rich lead is either desilverized by the Parkes process or, if sufficiently rich, is sent to the cupels directly. The copper matte is blown to blister copper in converters and refined electrolytically; or the converter copper is shotted by pouring in a thin stream into water; the shot copper is dissolved in shot towers or oxidizers by sulphuric acid; the copper is crystallized as blue stone, and the insoluble residue from the shot copper is treated in the cupel or slime furnace for the values contained in the copper.

A general rule not always observed in the treatment of very rich material is that it is often wise to make chemical perfection subservient to saving interest charges on the metals tied up in the process.

CHAPTER IX

THE METALLURGY OF COPPER

BY FRANCIS R. PYNE¹

The ores of copper may be classified under three main groups: native copper ores, oxide ores, sulphide ores. Native copper ores occur principally in the northern part of Michigan, and in three main forms: vein deposits, in which the copper occurs at times in enormous masses; amygdaloidal diabase, through which copper is disseminated; conglomerate, in which the cementing material consists, to a degree, of metallic copper. Native copper also occurs in China to a small extent. In Chile it occurs as copper barilla, in which the fine metallic particles are disseminated throughout sandstone.

The principal oxide ores are malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$; azurite, $2\text{CuCO}_3 \cdot (\text{Cu-OH})_2$; cuprite, Cu_2O ; atacamite, CuCl_2 ; and brochantite, $\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$. The oxide ores form much of the bulk of the South American and African copper supply. The principal sulphide ores are chalcocite, Cu_2S ; chalcopyrite, $\text{Cu}_2\text{SFe}_2\text{S}_2$; covellite, CuS ; bornite, $3\text{Cu}_2\text{SFe}_2\text{S}_2$; and to these should be added copper-bearing pyrite, FeS_2 .

The sulphide ores, however, furnish the bulk of the copper supply of the world, though the oxide ores are of importance. The advent of the flotation process of concentration followed by the development of selective flotation has virtually eliminated the direct smelting of ores and has substituted, therefor, the high-grade concentrate resulting from the practice of flotation concentration prior to smelting.

Smelting of Sulphide Ores.—In the smelting of sulphide ores, which may be considered as mixtures of copper and iron sulphides accompanied by siliceous or basic gangue, advantage is taken of the strong affinity of copper for sulphur and its weak affinity for oxygen, in comparison with the other bases in the ore. The object of smelting is to cause by fusion the conversion of the gangue into as valueless a slag as possible by the addition of proper fluxes, and at the same time to concentrate the copper and other valuable constituents of the ore into a small amount of high-grade material for further treatment.

Two important materials are formed during the smelting of copper-sulphide ores: (1) the slag produced by the combination of the gangue of the ore and the added flux; (2) the matte which is the product of the fusion of the metallic sulphides. Of these two products, the slag receives the first consideration of the metallurgist, because the sulphides melt readily under almost any circumstances, but unless the slag-forming constituents are properly proportioned serious difficulties will result.

A satisfactory slag must possess the following qualifications: (1) It must be as economical as possible, and to this end the other qualifications are subordinated, as a scientifically perfect slag may in the end be so expensive that any margin of profit is wiped out in its cost. (2) It must be sufficiently liquid to flow freely, but should not require an excessive amount of fuel to produce this condition. (3) The specific gravity should be sufficiently below that of the matte to permit the latter to separate thoroughly from it.

¹ Consulting engineer, Elizabeth, N.J.

The type of slag to be made depends, of course, on the slag-forming constituents available, and on the following general properties of the silicates.

Subsilicates.—While these slags are very fluid, they have a high formation temperature, and the specific gravity is so high as to make clean settling difficult, thus causing high metal losses. In addition, they are very corrosive and destructive to furnace and settler linings. Their formula is $(\text{FeO})_2\text{SiO}_2$.

Monosilicates.—These are quite fluid, but have a high formation temperature and are of sufficiently high specific gravity to make clean settling difficult. Basic silicates have a high dissolving power for metallic sulphides and thus tend to increase the metal loss in the slag.

Sesquisilicates.—These are mixtures of monosilicates and bisilicates, and are generally employed in smelting operations. They are sufficiently fluid to flow freely, the formation temperature is not excessive, and the specific gravity is sufficiently low to permit of clean settling with a consequent reduction of the metal loss.

Bisilicates.—These slags have a lower formation temperature, and the specific gravity is low. But they are more or less thick and viscous unless a high working temperature is carried in the furnace, so that the slag flows freely. Consequently, they require more fuel and thus are more expensive. When used they are, however, very clean slags. Their formula is FeO.SiO_2 .

Trisilicates.—These are seldom met with in any metallurgical practice as they require a very high temperature for their formation, and, as they are extremely viscous, require an excessive amount of fuel in order that they may flow properly.

As silicates with two or more bases are characterized by increased fusibility and fluidity, up to a certain point, it frequently becomes advantageous to have a small percentage of lime present. Frequently, on account of a shortage of iron, it becomes necessary to replace it with lime to a considerable extent, and this generally adds to the cost of the slag.

The amount of matte formed is dependent on the amount of available sulphur in the ore. By available sulphur is meant that sulphur that is present when the temperature of the furnace is such that chemical activity commences between the copper, iron, and sulphur.

When the raw sulphides are subjected to heating in a neutral atmosphere, any sulphur in combination with copper in excess of the compound Cu_2S will be expelled, and the product of fusion will be Cu_2S , which may be said to be the stable compound of copper and sulphur. Similarly with the iron sulphides, any sulphur in combination with iron in excess of the compound FeS will be expelled, and a fusion will result in the formation of this compound. Should, however, the heating be carried to a point somewhere between 1200 and 1500°C., a further amount of the sulphur is volatilized and an equivalent amount of metallic iron is set free, giving a compound that may be written FeFeS , which is of great importance in pyritic smelting.

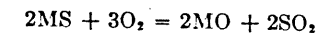
From the above it is seen that chalcopyrite, $\text{Cu}_2\text{SFe}_2\text{S}_2$, will lose about one-quarter of its sulphur by heat alone; covellite, CuS , will lose half of its sulphur; bornite, $3\text{Cu.SFe}_2\text{S}_3$, will lose one-sixth of its sulphur, and pyrite, FeS_2 , half its sulphur. For all practical purposes, matte may be considered to be a mixture of Cu_2S and FeS in varying proportions. It is also an excellent collector of gold, silver, and the other precious metals.

An ore high in sulphur and iron, but low in copper, will, upon fusion, produce a matte containing so low a percentage of copper that its subsequent treatment would, under ordinary circumstances, cost too much, and as it is the object of the metallurgist to concentrate the copper in his products up to the most economical point, steps must be taken to reduce the amount of sulphur available for the formation of matte and lower the amount of the latter produced per ton of ore smelted.

Such reduction may be accomplished in two ways, by an oxidizing roasting, or by subjecting the ore to an oxidizing fusion. When the ore occurs as massive sulphides, the latter method is frequently used where conditions make it economical; when the ores are not massive, the oxidizing roast is the predominating method.

Roasting is the heating to an elevated temperature, without fusion, or at least only with incipient fusion, of ores or metallic compounds in contact with oxidizing materials, in order to produce a chemical change or to eliminate a component by volatilization. In copper metallurgy, the oxidizing material is the oxygen of the air, and the object is the partial elimination of the sulphur in the ore.

When a metallic sulphide is heated to a sufficiently high temperature with access of air, sulphur dioxide is formed together with a metallic oxide.



Proper oxidation requires a temperature sufficiently high to produce the necessary affinity between the oxygen and the sulphur, but it must not be so high as to cause the surface of the ore particles to melt and form a protecting layer which retards the oxidizing action and may even cause it to cease. This temperature may be obtained by the combustion of extraneous fuel or by the heat of oxidation of the constituents of the charge.

A second requirement for proper oxidation is a constant and abundant supply of air in immediate contact with the surface to be oxidized. The necessity for an abundant supply is due to the fact that the oxidizing power of the air is lowered out of all proportion when diluted by the products of oxidation. In other words, if the air for oxidation is diluted with its own volume of gaseous products, the oxidizing effect of the resulting mixture will be much less than half the oxidizing power of pure air. The more rapidly the gaseous products are removed and replaced by pure air, therefore, the more rapid will be the roast.

The speed and the thoroughness of the roast are also governed by the size of the particles in the roaster. It is obvious that the finer the ore is crushed, the greater will be the surface exposed to the oxidizing influences. However, as fine material always results in losses through handling, flue-dust losses, etc., it will be seen that there is an economical point where the increased speed of roasting will be offset by the losses in material, the recovery of which necessitates expensive installations. The usual charge to a roaster consists of a mixture of relatively coarse and fine particles, and the roast is carried to a point where the overroasting of the fine particles balances the underroasting of the coarse particles, so that the final mixture from the roaster gives the desired sulphur content. The various types of apparatus used in roasting copper ores may be roughly classified as follows: heaps, stalls, cylindrical furnaces with superimposed hearths, blast-roasting apparatus. These methods will be found described at length in Chap. X of the first volume, "Principles and Processes."

Types of Smelting Furnaces.—Flotation concentrates constitute the major portion of the modern smelter's intake. Such concentrates consist of finely divided particles and range from 20 per cent copper upward to 30 or even 35 per cent. As a consequence, the blast furnace has become relatively obsolete, being almost universally supplanted by the reverberatory furnace.

The blast furnace is used mainly for the treatment of coarse ores over 1 in. in diameter, though in many cases much finer ore than this is treated successfully; however, the development of the modern reverberatory has progressed to the point where it has often been found to be more economical to crush the coarser ore to $\frac{1}{4}$ in. and treat in the reverberatory rather than in the blast furnace.

The early types of blast furnace were constructed of brick, and the molten products were collected in a crucible located at the lowest point of the furnace. This type of

furnace had two great disadvantages in addition to its small capacity. These were the destruction of the shaft at the smelting zone, and the impossibility of making a clean separation between the slag and the matte.

The first of these difficulties was overcome by the adoption of the water jacket, which not only eliminated the corrosion, but also permitted a higher temperature to be carried, resulting in a more fluid slag. The second difficulty was solved by the use of the external settler, which not only gave an efficient separation between the slag and matte, but also allowed the speed of the furnace to be greatly increased.

The modern blast furnace consists essentially of a long, narrow, water-jacketed shaft. The dimensions, particularly the length, vary considerably, being proportioned to the capacity of the furnace. The size of furnaces is expressed in terms of the dimensions at the tuyère level. The width, being limited by the ability of the blast to penetrate the charge, is generally 44 to 48 in., though some furnaces are as narrow as 30 in., and others as wide as 56 in. As the width is practically fixed within narrow limits, the only manner in which capacity may be obtained is by increasing the length, and present-day furnaces have lengths of 180 in. to as much as 1044 in., in the case of the huge Anaconda furnaces. The capacity of blast furnaces depends greatly upon local conditions but may be said to vary from 4.5 to 9.0 tons per sq. ft. of hearth area per day. The bottom plate of the furnace is generally a heavy ribbed cast-iron plate, supported by jackscrews. Upon this is laid a layer of firebrick, though special circumstances may require the use of silica or chrome brick. Resting on the bottom plate are heavy cast-iron plates bolted together, forming the walls of the crucible. These are generally heavily ribbed to ensure the necessary strength and are lined with the same material as is used on the bottom. In some instances, the walls of the crucible are formed by a set of water jackets, but the usual practice is to have the lower tier of water jackets rest directly upon the bottom plate, the lower ends being below the level of the matte and slag to prevent their burning through in case sediment collects in the water space.

When the blast furnace is started, the radiation from the bottom and through the water jackets forms a crust of chilled material which remains permanently. This crust adjusts itself to the operations of the furnace. If it wears down, the increased radiation soon restores it to the proper thickness, while if the furnace cools down the radiation is decreased, the bottom builds up, but when the furnace is once more at proper heat, the additional thickness is soon melted off.

The water jackets are generally in two tiers. The lower jackets rest either on the crucible plates, or, as has been stated, directly on the bottom plate. The upper tiers are suspended from I beams which carry the furnace superstructure. The upper jackets rest on the top of the lower jackets. The lower side jackets are given a slope toward each other to form a bosh, the upper and end jackets being vertical. The amount of bosh depends on the amount of reducing action desired, as the greater the amount of bosh, the greater will be the reducing action. The water jackets are constructed of flanged steel plate, the inner side being $\frac{5}{16}$ to $\frac{3}{8}$ in. thick, the outer side being somewhat thinner, $\frac{1}{4}$ to $\frac{5}{16}$ in. The water space between the sides of the jacket varies from 3 to 5 in. The jackets are stiffened by means of angle iron running vertically in the water space. Each jacket has its individual feed and discharge pipes for the cooling water, and where water is plentiful each jacket may be on a separate circulation, but where water is scarce the outlet of the lower jackets may be fed to the upper jackets.

The lower side jackets are pierced for the tuyère openings, there being usually three tuyères to each jacket. The opening is usually 4 to 6 in., and a steel thimble having a slight taper is welded to the inner plate and riveted to the outer plate. The tuyère pipes are generally of cast iron, and are bolted securely against the jackets, any leak-

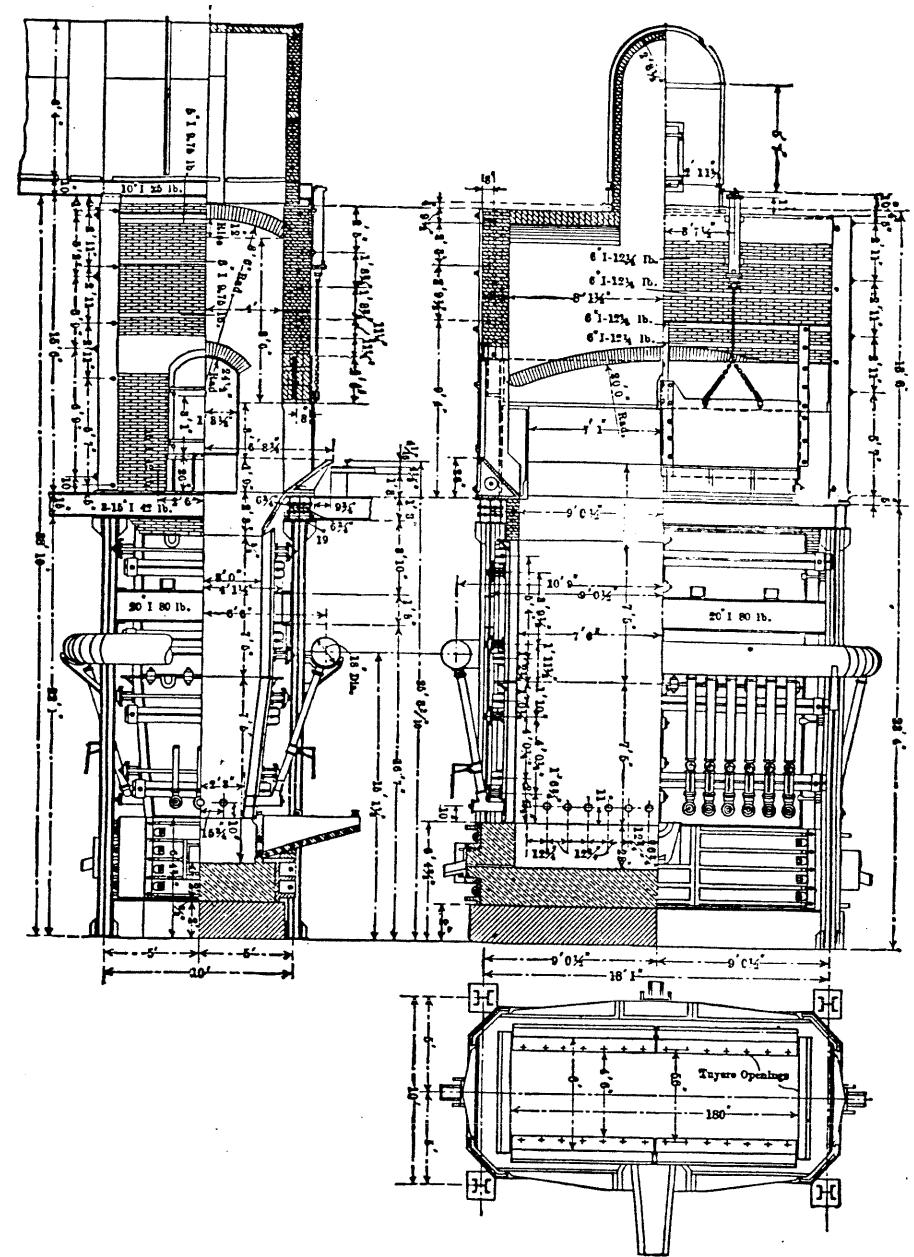


FIG. 1.—Typical copper blast furnace.

age being prevented by asbestos packing. There is usually a cap on the outer end of each tuyère pipe, which is readily removable to permit of punching the tuyères when necessary.

The tuyère pipes are connected by short branches to the main bustle pipe which carries the main air supply, the amount of blast to each tuyère being regulated by means of a valve. The volume of air required by the furnace varies widely, published figures being 190 to 400 cu. ft. per min. per sq. ft. of hearth area at a pressure of 32 to 40 oz. It is probable that the variation in these figures is due to their being derived by taking the revolutions per minute of the blowers or the piston displacement, neither of which is accurate, owing to the great amount of leakage.

The breast jacket is located either in the side or the end of the furnace, the location being largely determined by the available floor space and the general arrangement of the plant. It contains the opening for the removal of the molten products of the furnace and is securely attached to the adjoining jackets. The slag spout conveying the slag and matte from the furnace to the settler is fastened to the breast jacket in such a manner as to permit of its ready removal when required with minimum delay to the furnace operations. The spout may be constructed of wrought iron, steel, copper, or bronze, and is water-cooled. The blast is trapped by having the discharge end of the spout about 18 in. above the opening in the breast jacket, so that as the molten material from the furnace rises in the spout there is sufficient head to overcome the pressure of the blast. The shape of the slag spout depends upon the fancies of the designer of the furnace, there being many different designs in use, all of which appear to be giving satisfaction.

The jackets generally carry the shaft of the furnace to the level of the charging floor, though in some instances they are surmounted by several courses of firebrick. Just below the charging floor there is generally a set of feed or apron plates for the purpose of distributing the charge uniformly in the furnace by directing the fine material toward the center of the shaft while permitting the coarse material to fall along the sides. In many furnaces, however, these plates are omitted owing to local conditions making their use unnecessary.

Above the level of the charging floor is the superstructure of the furnace with the arrangements for feeding the materials of the charge and the removal of the furnace gases. There are many modifications in the design of the superstructure. In many cases it is of brick to a height of 12 to 14 ft. surmounted by a steel hood for the removal of the gases. In other plants the entire superstructure is of steel and occasionally water-jacketed.

The general practice of charging is through openings in the sides of the superstructure, which may or may not be kept closed by doors between charging. With the development of mechanical charging devices the gases are in some instances drawn off below the point of charging, particularly where the gases are utilized in the manufacture of acid. Care should be taken to keep the charge openings closed between charges on account of the great leakage of air that would otherwise occur, with its consequent detrimental effect on the draft of the furnace.

Air- or water-cooled steel hoods have marked advantages over the brick hood on account of the ready removal of accretions therefrom, and there seems to be less tendency for these accretions to form on this type of hood.

The furnace gases, on leaving the hood, pass through a downcomer of brick or steel, then to some sort of a settling chamber to remove the coarse particles of dust, and thence to the stack. The recovery of the flue dust is a matter of serious importance, and the methods used will be discussed at a later point.

The settler serves not only as a means for separating the slag and matte by reason of the difference in their specific gravities, but also as a reservoir for the storage

of matte until such time as it may be required. A plant that treats its own matte, therefore, requires a larger settler than does one that casts its matte directly into molds for shipment to some other plant for treatment. The settler is circular or oval, depending on local conditions and the plant layout, and consists of an iron shell lined with refractory material. The diameter may be as great as 26 ft., though 18 ft. is the usual dimension, the depth being 4 to 5 ft. The lining material varies greatly and depends on the grade of the matte, and character of the slag, the most rapid wear being occasioned by the very corrosive and fiery low-grade mattes usually accompanied by basic slags. A high-grade matte and an acid slag seldom cause much trouble through corrosion. The settler lining, where there is little corrosion, may be made of firebrick or silica brick; where corrosion is feared, the lining is generally of magnesite or chrome brick, or a combination of the two. Frequently, chromite or chrome ore is rammed into place and faced with a row of bricks to hold it in place until the heat of the molten material sinters it together. The lining is frequently protected by spraying water on the steel shell of the settler; this keeps the outside cool and causes a crust to form on the lining.

The roof of the settler is formed by the chilling of the slag, amounting to a thickness of several inches except at the point where the molten stream enters and leaves. The working platform was formerly this chilled crust but is at the present time a steel platform directly over the settler.

The slag overflows are constructed of cast iron coated with clay or other material, and are situated as far away from the entrance as possible, thus affording more time for settling. In many cases these overflows are situated at the side of the settler, due to the arrangement of the plant. The slag quietly flows out of the settler, and through these overflows into slag cars by which it is conveyed to the dump, or else it may be granulated by means of a strong stream of water, which not only granulates it but also carries it through launders to the dump.

The matte is withdrawn from the settler through tapholes situated close to the bottom. There are generally two of these holes, though many plants have but one. The hole in the wall of the settler is $1\frac{1}{2}$ to 2 in. in width and may be lined with chrome brick. Opposite this opening and attached to the shell of the settler is a copper or iron frame in which is securely wedged the tapping plate, which may be either iron or copper. The tapping plate has a 1-in. hole in the center into which a clay plug is rammed. A steel tapping bar is rammed through the clay plug until it almost reaches the matte and remains in that position until the tap is made. This is accomplished by withdrawing the steel bar by sledging against wedges held in place on the bar by rings. The matte flows from the taphole into the matte launder of cast iron, thickly coated with clay to protect it from corrosion, and from there into the ladle, which is usually of steel lined with cement and clay. During the tapping the workers are protected from the heat and splashes of matte by means of a slotted sheet-iron door which is swung out of the way when not required.

The charging of the blast furnace is accomplished in a number of ways. Hand charging gives the best regulation of coarse and fines and also possibly effects a saving of coke. It is frequently used up to capacities of 300 to 350 tons per day and in some cases even higher. It, however, is expensive and too slow for the average modern blast furnace smelting 600 to 700 tons per day and has, therefore, been superseded by some form of mechanical charging, particularly as the larger furnaces are less sensitive to slight irregularities in the charges than the smaller furnaces.

The general plan in use at the present time is to charge the furnace from side dump cars, varying greatly in their design, which are brought to the furnace in a train by a locomotive, and travel on tracks on each side of the superstructure. The contents of

the car may be dumped at one point, or the car may be moved along the length of the furnace while being dumped in order to distribute the charge.

Another scheme provides for the charges being brought to the furnace in cars and dumped on the charging floor from which they are pushed into the furnace by a mechanical pusher. At Granby, the furnaces were charged by pushing the charge cars into the furnace at the ends, from which they ran on tracks inside the furnace to the point of discharge. This gave a straight fall of material and provided good distribution.

In some plants the coke used for fuel is mixed with the charge and then sent to the furnace, but the usual practice is to charge it separately, and the utmost endeavor is made to keep the consumption of coke at a minimum, although this is not always easy to do, as the average furnaceman considers coke as a panacea for all ills.

Sizes of modern blast furnaces are shown in the following table:

	Area, inches	Blast, ounces	Capacity, tons
United Verde.....	48 by 320	40	950
United Verde Extension.....	48 by 312	30	600
Mason Valley.....	66 by 420	33	1,000
Calumet and Arizona.....	48 by 480	35	900
Garfield.....	48 by 240	40	600
Tacoma.....	45 by 261	35	650
Anaconda.....	56 by 612	40	1,400
Anaconda.....	56 by 1,044	40	2,500

The modern furnaces are vastly more efficient and economical than those formerly in use. Owing to the large amount of material in the furnace, they are less susceptible to slight irregularities. There is a saving of fuel, possibly amounting to 10 per cent, and there results a higher furnace temperature, giving hotter slag and enabling a more siliceous charge to be run. There is a marked decrease of incrustations, which eliminates the necessity for much barring. It has been found possible to change a leaking jacket without shutting the furnace down. This is accomplished by blocking off the tuyères in the leaking jacket as well as those in the adjacent jackets and allowing a crust to form that is sufficiently strong to support the charge during the short period necessary to make the change.

There are three distinct processes in blast-furnace smelting: (1) The reduction process, in which a considerable percentage of coke, 15 per cent, is used. The blast oxidizes the carbon of the coke and but little of the sulphur in the ore. This is the process most generally used. (2) The pyritic process, in which raw massive sulphides are smelted in a highly oxidizing atmosphere without the addition of carbonaceous fuel. The heat generated by the oxidation of the sulphur and iron is sufficient to maintain a continuous operation. (3) The partial- or semipyritic process in which sufficient heat is not generated by the oxidation of the sulphides and carbonaceous fuel is added to the charge in just sufficient quantity to overcome the deficiency.

The Reduction Process.—This process is characterized by the use of carbonaceous fuel as the principal source of heat. The sulphur content of the charge is sufficient to form the desired matte, and any oxidation is generally undesirable.

The percentage of coke, which is the usual fuel used, varies from 12 to 15 per cent. An excessive amount of coke is liable to cause a reduction of iron from the slag, while with a shortage the furnace becomes chilled and suffers a loss of tonnage.

The use of such an amount of coke means that the furnace always contains a large mass of glowing coke for a considerable distance above the tuyères, and consequently the oxygen in the blast is consumed almost immediately, resulting in a strong reducing atmosphere. Such being the case, it is readily seen that any sulphides present will melt down unchanged and form matte. An ore high in sulphur would, therefore, yield a large amount of matte which is expensive to treat, and it is clear that little would be gained by the reducing smelting of such an ore, and that a portion of the sulphur must be eliminated by a roasting process previous to the treatment in the blast furnace, or else the sulphides may be mixed with oxide copper ores to increase the grade of the matte. A certain oxidation of sulphur may be accomplished in the blast furnace by keeping the ore column low and increasing the blast, but such procedure generally results in a very hot top and high temperatures of the waste gases and, in general, is not economical.

Regarding the chemistry of the process, the blast entering through the tuyères oxidizes the carbon of the coke to CO_2 , which is then partly reduced to CO by the glowing mass of coke in the furnace, the resulting gases being a mixture of CO , CO_2 , and the nitrogen of the air. As these gases rise in the furnace and reduce the oxidized materials, the percentage of CO_2 increases and will predominate in the waste gases. Any remaining CO is usually burned to CO_2 in the upper part of the furnace.

As the charge descends in the furnace, its moisture is driven off almost immediately, followed by the decomposition of such carbonates as may be present. At a lower point the oxides and silicates of copper will be reduced, and on coming into contact with metallic sulphides will be converted into copper sulphides which, with any existing sulphides, melt and flow downward to the crucible, collecting the silver and gold as they descend. Ferric oxide, Fe_2O_3 , is reduced to ferrous oxide, FeO , which combines with the silica to form slag as does any lime or other flux added to the charge. When the molten materials have collected in the crucible below the tuyères, the various sulphides adjust themselves to form the proper matte, and likewise the various slag components adjust themselves to form the proper slag.

The Pyritic Process.—The feature of this type of smelting is that the heat necessary to conduct the operation is furnished by the oxidation of the constituents of the ore, little or no extraneous fuel being used for this purpose. Up to 2 to 3 per cent of coke may be added to the charge purely as a preheating medium and possibly to secure a more open charge. It certainly never reaches the smelting zone.

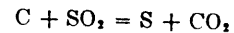
The essential requirements for pyritic smelting are siliceous material which is high in free silica, and heavy pyrite ore. It is necessary for as much of the silica as possible to be in the free state in order that it may combine with the ferrous oxide at the instant of its formation. Combined silica is unsuited to the pyritic process as it is already united with one or more bases and consequently requires a large amount of heat to break up the existing combinations and form new ones with the ferrous oxide, and generally in the pyritic process there is not any too large a margin of heat.

The pyrite ore not only furnishes the heat for the operation, but also the sulphur required for the matte, and it must consist largely of iron pyrites, as any oxidation of the copper sulphides would result in the slagging and consequent loss of the copper oxides.

As the charge sinks in the furnace, any moisture present is quickly driven off, followed by the dissociation of the limestone added as flux. The free sulphur in the sulphides will be expelled as heavy fumes of elemental sulphur, and at a point just

above the smelting zone the pyrite has been changed to FeFeS , which is the true pyritic fuel of the process.

The blast entering the furnace through the tuyères strikes the hot fused sulphides, oxidizing the Fe to FeO and the S to SO_2 . The FeO simultaneously unites with the silica to form a ferrous silicate slag, while the SO_2 rises through the charge and preheats it assisted by the oxidation of such coke as may be present:



The matte collects below the tuyères, as does also the ferrous silicate slag after uniting with the lime to form the final slag. The fused mixture then flows through the spout to the settler.

The grade of the matte produced and the acidity of the slag are controlled by the volume of air blown into the furnace. A reduction in the amount of air will cause less of the sulphide to become oxidized, and the grade of the matte will, therefore, be lowered. At the same time the slag will become more siliceous, as less iron is oxidized, and this condition will interfere with the process unless the amount of siliceous material in the charge is reduced. On the other hand, any increase in the volume of air will oxidize an additional amount of iron, raising the grade of the matte and increasing the iron in the slag unless additional silica is provided.

A peculiarity of the pyritic process is the artificial bosh formed on the side and end walls of the furnace. This contracts the smelting area to a long, narrow slit. This bosh is composed of fragments of quartz struck together by slag or by superficial softening, and seldom contains matte. Its position in the furnace is not fixed, but varies under different conditions.

While in reducing smelting the tuyères are bright, in pyritic smelting they are dark and are bridged across. It has been stated that a bar can be passed through the furnace from one tuyère to the opposite tuyère and be cool when withdrawn. This indicates that the zone of fusion is well above the tuyère line and that the molten material passes through channels between the tuyères.

Partial pyritic smelting is used when the available sulphide ores are not massive but consist of pyritic material disseminated throughout the gangue, which is generally low in free silica and which may contain some alumina. Such ores are not capable of furnishing by themselves sufficient heat for the continuance of the process, and it is, therefore, necessary to add carbonaceous fuel. In some instances it has been found advantageous to preheat the blast, as thereby a saving is accomplished in the amount of fuel used.

In the partial pyritic process the slags are rather low in iron, as the presence of coke requires much of the oxygen of the blast for its combustion and there is less available for oxidizing the iron in the sulphides. The excess silica will, therefore, have to be taken care of by the use of lime. In order that there may be any considerable pyritic effect, a large amount of blast is necessary, and this usually results in the furnace having a hot top.

The smelting zone is nearer the tuyère level and is not so contracted as in pyritic smelting, but is higher and more contracted than in reducing smelting. The tuyères are frequently dark and require a great deal of punching to keep them open.

The principal features of the blast furnace for the treatment of coarse ores are that its construction is simple and the erection is comparatively inexpensive. Where small installations are required, they can be purchased complete and are easily transportable from one location to another. The furnace is easily started and shut down, and the operation is relatively cheap. The fuel consumption is low, and there is the possibility of utilizing the fuel value of the iron and sulphur in the charge, and the heat is efficiently communicated to the individual parts of the charge.

The blast furnace is exceedingly elastic in its operation, and changes in the ore supply are readily handled with little trouble. It is capable of handling practically every class of copper-bearing material in lump form, and, with modern sintering facili-

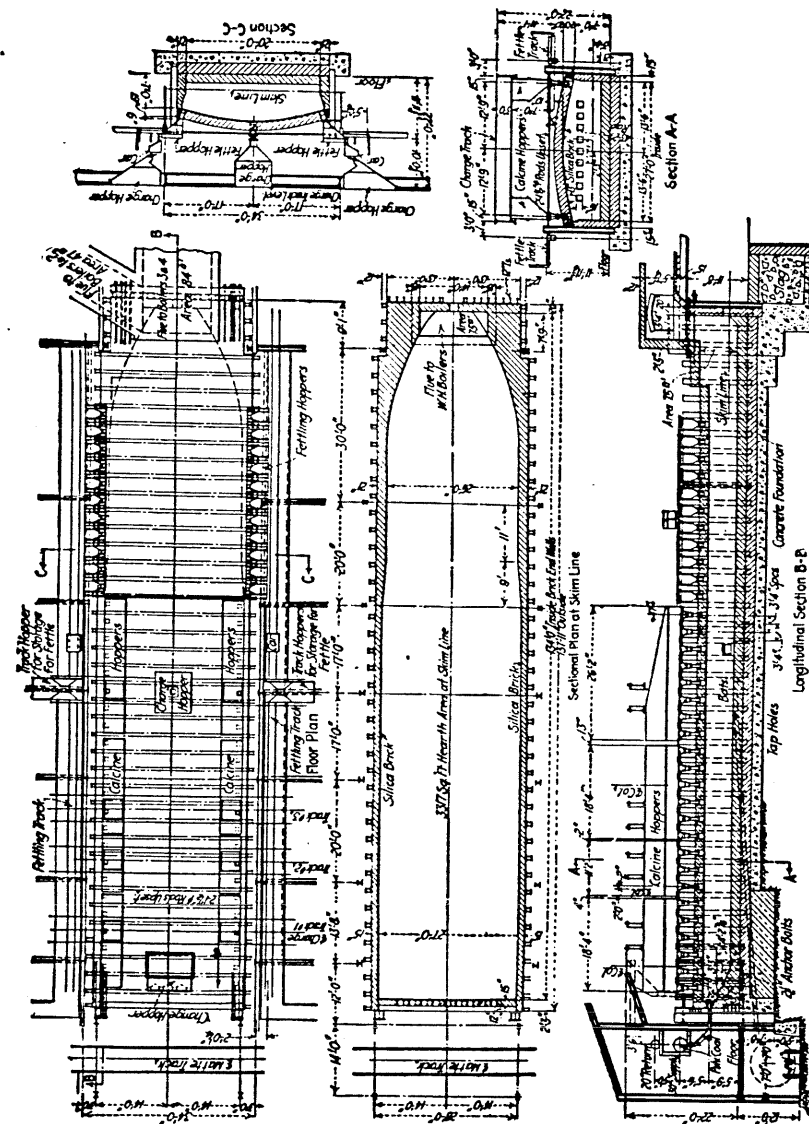


Fig. 2.—Reverberatory smelting furnace at Nevada Consolidated smelter.

ties, much fine material can also be treated that would otherwise be uneconomical to handle.

The reverberatory furnace is used for the treatment of fine ores, and the fuel and ore are kept separate, the former being burned in a separate compartment from which the flame and hot gases pass over the ore, being guided in their course by a

more or less horizontal roof. The heating of the ore is accomplished by the radiation from the roof and side walls rather than by direct contact with the hot gases.

It is particularly suitable for fine materials on account of the relatively quiet atmosphere, due to there being no blast, and there are greater opportunities for the settlement of dust than in the blast furnace. As the furnace atmosphere is neutral, or very nearly so, it has little or no influence on such reactions as occur in the furnace, and it, therefore, follows that the reverberatory is purely a melting furnace.

The functions of the furnace are that it shall melt down ore and flux as rapidly as possible with a minimum of heat loss; it should permit the formation of matte and slag from the mixture of oxides, sulphides, and sulphates in the charge; and the temperature must be sufficiently high to render the matte and slag perfectly fluid in order that there may be complete settling with a minimum of loss in the slag.

In order that the furnace may melt as rapidly as possible, it is necessary that there be a good draft, in order that the great volume of gases that have been cooled down by their contact with the roof, walls, and charge be replaced as speedily as possible by fresh hot gases.

The heat losses are kept at a minimum by the elimination of side-door charging with its consequent admission of large volumes of cold air; the walls and roof are made as thick as economically possible to reduce the radiation losses.

The heat of the gases is utilized to the greatest possible extent by making the furnace as long as will permit the charge being kept in a fluid condition without an excessive consumption of fuel, and such heat as necessarily leaves the furnace as sensible heat in the waste gases is, to a large extent, recovered by passing them through waste-heat boilers.

The hearth is of silica sand 24 to 30 in. in thickness. The sand is given a preliminary calcining and is then leveled and sintered into place by long, continuous firing. As the modern practice is not to drop the charge on the hearth, but on a bath of molten material which is supported by the hearth, there is little wear on the latter, resulting in a very long life. Crushed quartz may be used instead of sand.

The reverberatories of the new Morenci plant of the Phelps Dodge Corp. are 110 ft. \times 31 ft. 3 in. outside the walls, which is somewhat smaller than furnaces built some years ago, some of which were 130 ft. long. These furnaces are designed to smelt 650 tons of charge per day. The walls are stepped or tapered from 1 ft. minimum at the top to 4 or 5 ft. maximum thickness at the bottom. Construction is silica brick, lined with magnesite except in the charging zone. Silica brick is used for the arch, which is 20 in. thick, 35 ft. in radius, and is horizontal for its full length. It is 9 ft. high at the spring line, measured from the top of the silica bottom, which is at the same level as the reverberatory building floor. A 2-ft. layer of crushed silica is used for the bottom. Below this is a layer of poured slag 8 ft. thick near each end of the furnace and 4 ft. thick in the intermediate zone. The 8-ft. depth is provided in order to bury the lower tie rods for resisting endwise expansion of the furnace.

One large longitudinal tie rod runs the full length of each side of the furnace, and the buckstays are tied across with horizontal tie rods in the usual manner. Heavy concrete walls take the bottom buckstay thrust and confine the silica and slag bottom. Pilasters, 13 in. square, at the buckstays space these members from the face of the wall.

A few years ago the amount of iron sulphide in the flotation concentrates practically forced the use of roasters, and the calcines were usually delivered to the reverberatory as hot as possible. The improvement in grade of concentrates due to differential flotation is such that in the new Morenci plant roasting has entirely been dispensed with and the concentrates are charged wet through a series of charge spouts at 4-ft. centers along the furnace roof. They contain about 9 per cent moisture. Such coarse ore as is suited for direct smelting, which would formerly have been treated in

blast furnaces, is crushed to $\frac{1}{4}$ in. and added to the reverberatory charge beds. The necessary lime flux is also crushed and added to the beds.

The advantages of wet charging are the elimination of the roasting plant and the facts that there is no dusting in the furnace and that there is a great decrease in the accumulation of magnetite on the hearth. So far it has been limited to plants operating in mild climates and would probably offer great difficulties in cold climates.

Depth of the bath is nominally 3 ft. Three matte tap plates, for alternative use, are placed on each side of the furnace near the firing end, with the single slag tap in the side wall near the uptake flue. The slag launder branches to two openings over different tracks. The highly superheated bath readily gives up heat to the fresh charge, and it receives further heat from the radiation from the roof and quickly melts.

The resulting slag and matte now move toward the tapping end of the furnace and have ample time in which to separate cleanly. The slag may be tapped intermittently or allowed to flow off continuously, the latter coming more into favor as it results in cleaner slags. The matte is tapped from the fore part of the furnace, as required by the demands of the converters, in a manner similar to tapping a blast-furnace settler.

The fuel used in the modern large reverberatory furnace is gas, pulverized coal, or fuel oil, depending on the relative cheapness of the fuels. When pulverized coal is used, it is ground so that 80 to 90 per cent will pass a 200-mesh screen, and is blown into the furnace with about 15-oz. air pressure. The coal used may vary in ash content from 6 to 7 per cent up to as high as 15 to 20 per cent without giving trouble. The ratio of charge to fuel varies from 5 to 7 $\frac{1}{2}$. The burners are inserted directly in the rear wall of the furnace and several burners are used, four to six being the usual number. The type of burner varies in each plant with apparently equally satisfactory results.

When using fuel oil in the furnaces it is generally 17 to 19 Bé and is preheated to about 200 to 250°F. before burning, as this results in fuel economy. The amount of fuel oil used per ton of charge varies from 0.50 to 0.70 bbl. When as much heat as possible has been extracted from the gases, they are passed through waste-heat boilers for a further recovery. These are 500 to 750 b.h.p., and they frequently are connected to a common cross flue extending from all the reverberatory furnaces, so that in case of a shutdown of a furnace the boiler capacity will not be lost, and if a boiler is down for cleaning or repair the other boilers are available for the utilization of the waste heat. It has been found to be advisable to have the flues from the furnaces to the boilers slope slightly toward the furnaces, as otherwise trouble may be experienced from the accumulation of slag.

Natural gas is a highly efficient, clean fuel, but obviously its use is limited to localities adjacent to natural gas fields. Fuel oil and natural gas have an advantage over pulverized coal in that there is no ash which would increase the amount of slag.

In the new Morenci plant, two groups of four multiple-jet low-pressure gas burners fire through two rectangular ports. The burners are suspended from individual trolleys, permitting withdrawal from the firing position, and an oil burner accompanies each one, for emergency or auxiliary use. A suspended arch forms the top of the firing wall.

Following modern practice the 8 $\frac{1}{2}$ \times 23 ft. uptake flue is made as short as possible and branches to two waste-heat boilers. The flue bottom slopes steeply back toward the furnace to drain the slag. The roof and the back wall are of suspended construction, using magnesite brick. A solid brick damper can be dropped through a slot to cut off one boiler.

At a new Canadian plant, using suspended-arch construction, the width of the furnace is 35 ft. in the smelting zone. All Canadian plants are using side feeding, the

unsmelted charge being kept away from the skimming bay. The American Smelting and Refining Co. favors a deep-bath gun feed. Water-cooled jackets along the bath-line of deep-bath smelting furnaces appears to have become standard practice. Copper jackets with 1½-in. water coils have proved most satisfactory.¹ The use of about 3 per cent of bentonite has been found very helpful in making a silica slurry mixture that will adhere to brickwork. Magnetite sand is now (1943) being tried for reverberatory bottoms, with the hope that its higher specific gravity and lower coefficient of expansion, as compared with silica, will make it a decided improvement. The reverberatory is more independent of type slags than is the blast furnace. So far as reverberatory slags may be said to be typical, current practice appears to tend to a slag containing 37 to 38 per cent SiO₂, 39 to 40 per cent FeO, 4 to 6 per cent Al₂O₃.

In the reverberatory furnace any reducing action is performed by the sulphur in the charge. This reacts with the oxides and sulphates to produce metallic copper and sulphur dioxide. The metallic copper is then sulphurized by the sulphides of iron present, oxidizing the iron to FeO, which combines with the silica present to form the slag. The reverberatory furnace will make a higher silica slag than a blast furnace, owing to the higher available temperature. Any iron oxide, Fe₂O₃, present in the charge is acted upon by the sulphides and reduced to FeO, uniting with the silica.

The grade of matte produced by the reverberatory furnace depends upon the degree of roasting that the ore has received or the cleanness of the concentrate. If a higher grade of matte is desired, the roast is carried to a higher degree, and if the matte is too high, the roast is not pushed to the same completeness. In the roasting, care must be taken that no magnetic oxide of iron, Fe₃O₄, is formed, as such material forms a mush in the furnace and is difficult to remove. When it occurs, the remedy is to add a large amount of green sulphide ore to the charge, which will reduce the magnetite to FeO.

Comparing blast-furnace and reverberatory-furnace smelting, the former requires coarse ore in order to give the best satisfaction, little space is required, and the investment is low for any given tonnage. The fuel, though small in amount, is relatively expensive, and considerable power and a large amount of cooling water are required. Blast-furnace slags can be made between very wide limits, but the addition of a large amount of flux results in the production of a large amount of slag with a corresponding metal loss.

The reverberatory furnace is the most satisfactory and advantageous apparatus in which to treat fine ores, but it usually requires an extensive roasting plant and in itself occupies a large amount of space and locks up a large amount of valuable metal. Hence the investment is large for a given tonnage. While large amounts of low-priced fuel are used, a large proportion of the heat in the gases is recovered in waste-heat boilers and this greatly reduces the power cost. The amount of slag and, consequently, the metal loss are less than with the blast furnace. With the ever-increasing amount of fine ores to be treated, the reverberatory furnace is fast displacing the blast furnace, and it has been found advantageous in certain localities to use reverberatory smelting for coarse ores that under ordinary conditions would go to the blast furnace.

Converting.—When copper and other valuable constituents of the ore have been concentrated into the matte, and the worthless material disposed of as slag, the next step in the process is the removal by oxidation of the iron and sulphur of the matte. This is accomplished by transferring the molten matte to a refractory-lined vessel,

¹ WAGSTAFF, *Metals Tech.*, February, 1944.

known as a converter, and forcing thin streams of air through the liquid mass. The reactions involve the rapid oxidation of the iron and sulphur and the fluxing by silica of the iron oxide thus produced. The sulphur dioxide formed by these reactions passes off in the waste gases. The heat of oxidation is such that the materials are kept in a molten condition, and the temperature is maintained well above that necessary for the formation of the slag, so that the process is independent of heat from external sources. The copper, together with any silver or gold, is reduced to the metallic form and is cast into suitable shapes for transportation to the refinery for further treatment.

The converter is a cylindrical iron or steel vessel lined with refractory material. A conical mouth is provided through which the matte is introduced, the slag and blister copper withdrawn, and the gases pass to the stack. The air for the oxidation is introduced through the side of the converter by means of tuyères leading from a wind box attached to the outside and having a connection with the blast main.

The early types of converters were blown from the bottom, similar to those used in the steel industry, but this method was not a success, due to the chilling effect of the blast on the copper, which, when produced, sank to the bottom of the converter and froze in the tuyères, thus stopping the operation. This was remedied by raising the tuyères so that there was space for the copper to settle underneath the blast.

The refractory lining may be composed of either acid or basic material. The acid lining, though formerly universal, is practically entirely supplanted by the basic lining. The functions of the lining are to preserve the steel shell and form a receptacle for the molten materials, and to prevent radiation losses to the greatest possible extent.

In the acid lining the material used should contain the largest possible amount of free silica. The material generally used is low-grade siliceous ore, which, while it may not be so desirable metallurgically as quartz, is smelted for nothing, and the values recovered from an otherwise profitless material make the substitution economical. The ore is crushed and mixed with a binding material in a mill, and is pounded down hard in the bottom of the converter by tamping machines until it reaches to the proper distance below the tuyère level. At this point a steel or wooden form is placed in the converter, and the lining material is rammed around the form in layers about 6 in. in thickness. When the operation is completed, the form, which is sectional, is removed and the tuyère holes are punched in the lining. The hood is then inverted and lined and placed upon the body of the converter and securely bolted in place, the joint being covered with clay.

The freshly lined converter is now dried slowly by a wood fire, after which coke is added and kept burning by an air blast through the tuyères for 5 or 6 hr., after which the converter is ready for operation.

The basic lining is magnesite brick, the thickness varying from 9 in. at the top and sides to 18 in. along the tuyère line and bottom. The brick may be laid in magnesite powder and linseed oil, or sodium silicate may be substituted for the linseed oil. In order to furnish room for proper expansion, liners consisting of thin strips of wood are placed at intervals along the sides. After lining the shell, it is carefully warmed to prevent spalling and is then ready to be placed in the stand.

The air for oxidizing the sulphur and iron is admitted through tuyères usually 1 to 1½ in. in diameter, placed about 8 to 12 in. above the bottom. The tuyères are connected to a wind box having openings opposite each tuyère to permit of punching when necessary. These openings are provided with ball valves to prevent leakage of air while the converter is operating. The air is supplied at a pressure of 10 to 20 lb., depending upon the type of converter used and the depth of matte carried. The amount of air required will depend, of course, upon the grade of matte being

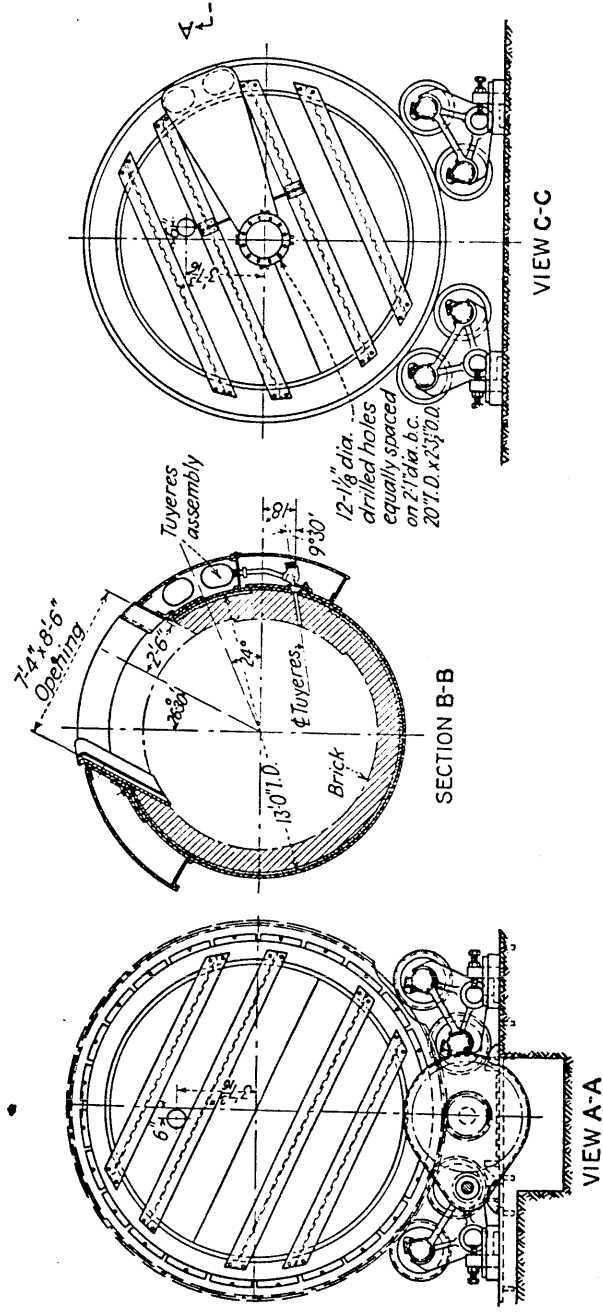


Fig. 3a.—Cross section, Peirce-Smith converter. (Courtesy of Traylor Eng. & Mfg. Co.)

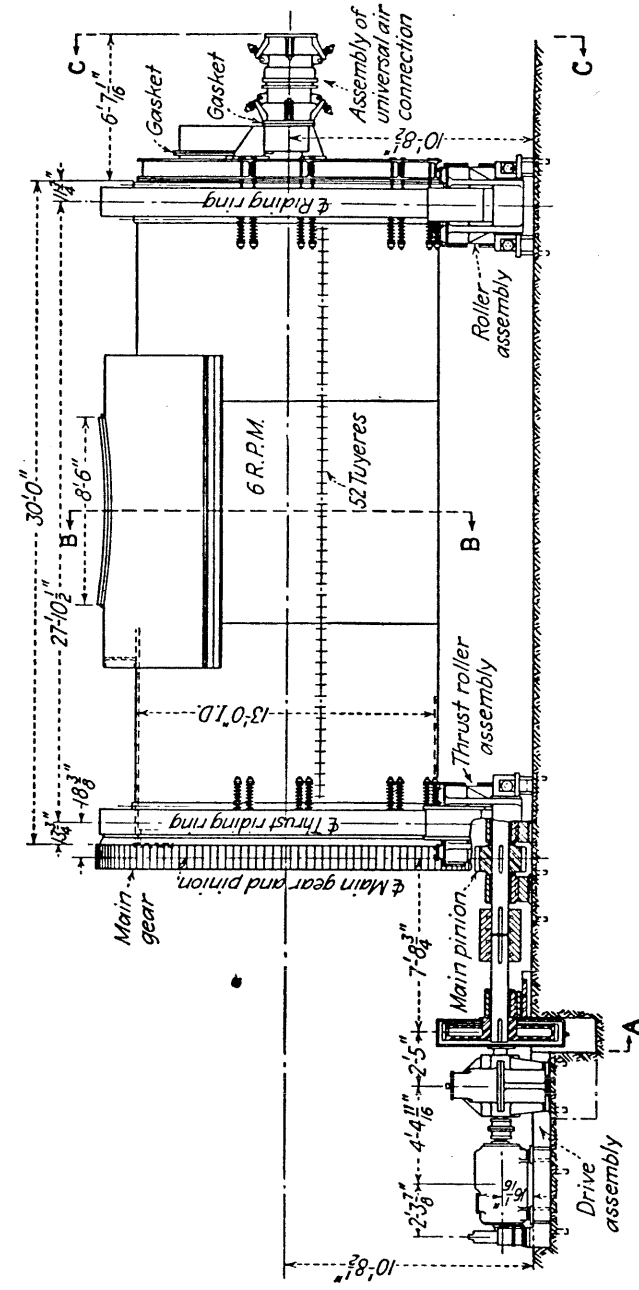


Fig. 3b.—Side view, Peirce-Smith converter, Morenci, Ariz.

converted, but will average 160,000 to 200,000 cu. ft. of free air per ton of blister produced for a 40-per cent matte.

The grade of matte that is most economical to treat in the converter depends upon the cost of the preceding operations. A low-grade matte, low in copper but high in iron, has the advantage of enabling a high temperature to be obtained owing to the fuel value of the FeS. On the other hand, the amount of iron that must be slagged requires a corresponding amount of silica, and produces a large amount of slag carrying considerable copper which is too valuable to waste and must, therefore, be re-treated for the recovery of the copper contents. The amount of copper per ton when using low-grade matte is relatively small, and the cost of treatment therefore high.

A high-grade matte, high in copper but low in iron, has the disadvantage of containing less heat, and there may be difficulty in maintaining the desired temperature.

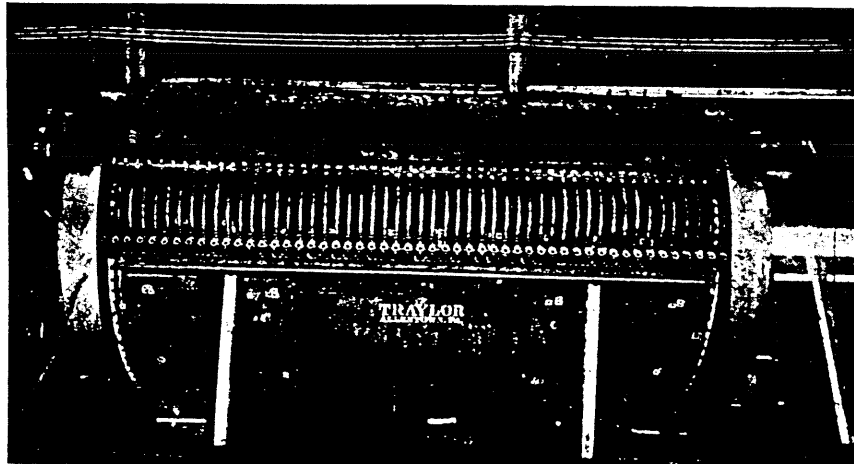


FIG. 4.—Peirce-Smith converter.

The amount of slag produced is decreased with a consequent lower re-treatment cost per ton of copper produced, and the cost of converting is reduced due to the larger amount of copper per ton of matte. The economical grade is reached, other things being equal, when the cost of fluxing the iron in the regular smelting operations is less than doing so in the converter.

The operation of acid converting is conducted by first heating the converter to the required temperature by the use of wood and coke. The proper amount of matte is then introduced through the mouth, the blast turned on, and the converter turned up so that the mouth is under the hood conveying the gases to the stack. The tuyères are now below the surface of the matte and the oxidation commences. There are two main stages in the operation: (1) the elimination of the iron, or blowing to white metal; and (2) the elimination of the remaining sulphur, or blowing to blister.

During the first stage the iron sulphide is oxidized to FeO, the sulphur oxidizing to SO₂ and passing off in the waste gases. The FeO immediately attacks the siliceous lining to form the slag. Any copper that may be oxidized is immediately resulphurized by reacting with the iron sulphide. As the oxidation proceeds and the iron is slagged, the matte remaining in the converter gradually approaches white metal (Cu₂S). This change may be followed by noting the character of the flame issuing from the mouth of the converter. At the start of the operation it has a reddish color

changing to a green, and as the white-metal stage approaches, to a pale blue. If, however, an impure matte is being converted, the flame indications are unreliable, and dependence is placed on the appearance of the layer of matte on the punch rod which is inserted in the tuyères to keep them open for the passage of the blast. When the white-metal stage has been reached, it is indicated by the working of the matte on the rod.

When the iron has been slagged, the converter is turned down, the blast shut off, and the slag skimmed into a ladle. In order to determine when the slag has been skimmed clean, a rabble is held under the stream and any white metal coming over will be seen by its working on the iron of the rabble. When the slag has been skimmed, a fresh charge of matte may be introduced and the operation repeated. This is known as doubling, and is done for several reasons. If the temperature of the charge is too low, there may be danger of freezing during the finishing blow; the fresh addition of matte, therefore, gives fresh fuel with which to raise the temperature. If the matte is low grade, there may not be sufficient white metal present to cover the tuyères and, therefore, more matte must be added. If the converter cavity has become enlarged, the same condition prevails, and sufficient matte is added until the amount of white metal remaining is sufficient.

During the second stage the sulphur in the white metal is oxidized, the sulphur passing off in the gases as sulphur dioxide, the oxidized copper reacting with the remaining white metal to produce metallic copper and sulphur dioxide. The copper settles below the tuyère level and collects any silver and gold that may have been in the matte. During this period the flame of the converter changes from a pale blue to reddish brown, and the metal on the punch rod becomes more and more coppery. When the charge is finished, the converter is turned down, the blast shut off, and the metallic copper poured into a ladle for casting, or it may be cast direct from the converter. The former practice is to be preferred, as the latter causes too much delay to the converter and keeps down the tonnage treated per day.

The main objection to the acid process of converting is the rapid destruction of the lining by the union of the FeO with the silica, the latter being the sole source of silica supply. The life of an acid lining is limited to a relatively few charges, depending on the grade of matte converted, a low-grade matte being more destructive than one of higher grade, due to the larger amount of iron slagged. The expense of constantly renewing the lining was heavy, and for years efforts were made to find a lining that would not be attacked by the iron. After many attempts and failures this was successfully accomplished by Peirce and Smith.

Basic-lined Converters.—The operation of converting in the basic-lined converter is similar to the acid operation as far as the reactions go, but the silica for slagging must be supplied from some external source. As the charge of matte is in the converter, the necessary amount of siliceous ore is added, the blast turned on, and the converter turned up. The flux is generally thoroughly dried before being added to the matte to avoid explosions, though in some plants the siliceous flux is blown into the converter and spreads out over the matte in thin layers and, consequently, does not have to be dried.

The basic-lined converter cannot be operated at the temperature of the acid converter on account of the destruction of the magnesite lining at high temperatures. The lower temperature required necessitates a great deal of punching of the tuyères. With a low-grade matte there is a greater heat liberation than when a high-grade matte is being converted, and great care is necessary that the bath be not overheated. Too high a temperature retards the converting, attacks the lining, and tends to warp the converter shell. On the other hand, too low a temperature makes the tuyère punching very difficult, makes a sticky slag, and is liable to cause the formation of

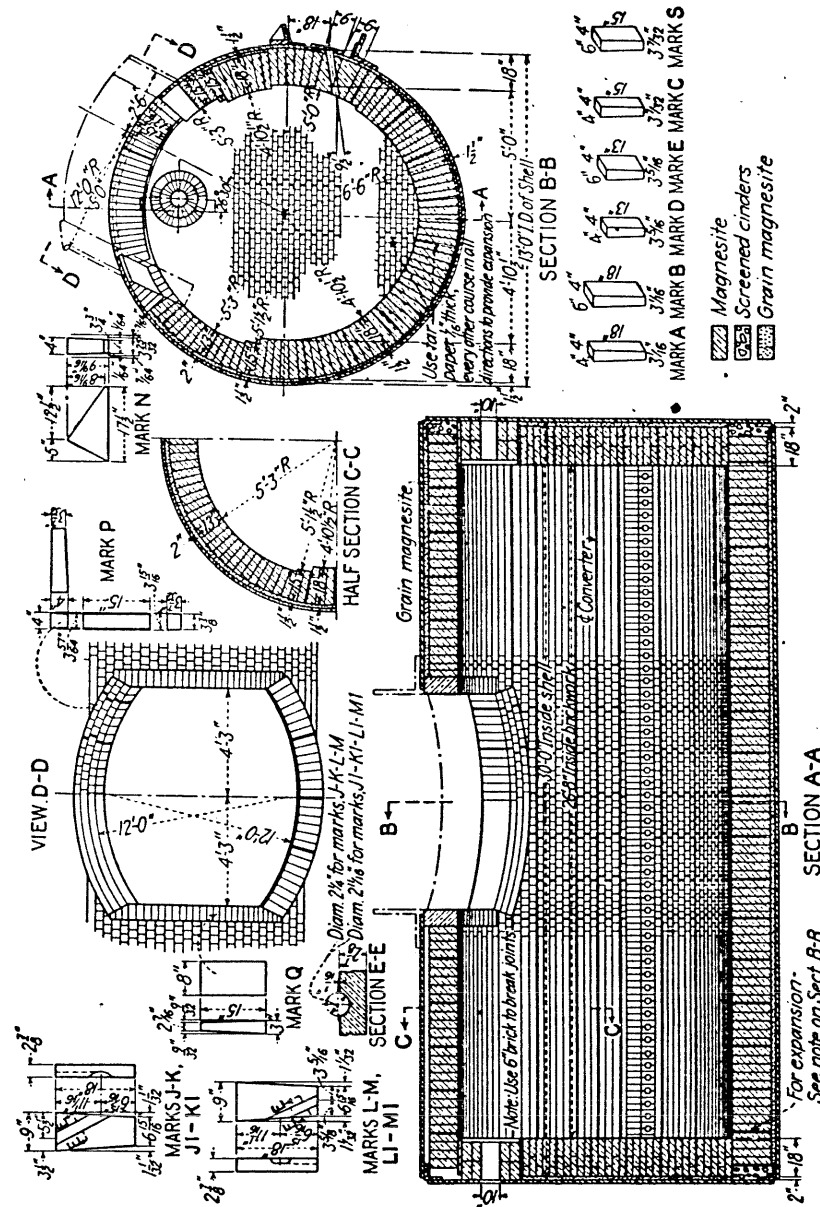


Fig. 5.—Lining of Peirce-Smith converter, Morenci, Ariz.

magnetic oxide of iron which builds up on the bottom and sides of the converter. Owing to the nature of the process, the basic converter operates at a lower temperature than the acid process, mainly on account of the large quantities of cold ore added as flux.

The critical stage of the operation is at the finish of the slagging period. If there is insufficient silica present to take care of the iron, magnetite will be formed, while an excess of silica causes a sticky slag. Magnetite is also caused by an insufficiency of silica during the blow to white metal, and this has been taken advantage of to give added protection to the lining. Wheeler and Krejci at Great Falls, Mont., patented a process of blowing a low-grade matte with either no silica or else a very small amount. This causes the iron to form magnetite, which covers the magnesite lining to almost any desired thickness and thus greatly prolongs the life. When this coating wears off in the course of the succeeding operations, it may be readily renewed during the next charge.

The main advantages of the basic converter over the acid converter are the greatly decreased cost of lining; the use of much larger converters, which make for labor and power economies; a lower-grade matte can be treated than in the acid converter; the copper in the slag is lower; low-grade ores can be used for flux that could not otherwise be treated profitably; there is less slop from the converters; and the copper is produced in a shorter time.

The slag from the converting process, containing as it does several per cent of copper, is too rich to be thrown away and is returned to the blast furnace or reverberatory, or may be treated in a slag-cleaning furnace. At some plants, it is the custom to pour the molten slag into the blast-furnace settler. This is done on account of the blast-furnace charge being so high in iron that the added iron from the converter slag is undesirable. The economy of this operation, however, is a disputed question as many metallurgists claim that the copper is not recovered to any great extent, but simply mixes with the great mass of blast-furnace slag and is lost.

Plant executives appear to rate the modern 13 × 30-ft. Peirce-Smith converter at 100 tons of copper per day for a 37 per cent matte, with an increase or decrease of 5 tons for each 1 per cent up or down in the matte tenor (within reasonable limits).

The Smelting of Oxide Ores.—Where oxide ores occur, such as in the Katanga district, these are smelted in blast furnaces with a large percentage of coke. The product is known as "black copper," and its composition depends on the impurities in the ore. A clean ore will give a high-grade copper, while, if much iron or nickel is present, these will be reduced and will lower the grade of the copper. Usually a small amount of matte is produced, owing to the sulphur in the coke or small amounts of sulphides in the ore. Where there is little or no sulphur present, the copper losses in the slag are apt to be high, while a small matte fall tends to clean the slags.

The blister copper produced from any smelting process is generally cast into slabs approximating 18 × 28 in. and 3 to 4 in. in thickness, weighing 300 to 350 lb. There is just sufficient draft to the slab to permit of its ready removal from the mold. At some plants, the practice still continues of casting the old type of Chile bar, which is about 8 × 20 in. with a thickness of 6 to 8 in. This type of bar is very difficult to sample properly, on account of the segregation of the silver and gold, and it is also a difficult pig to handle easily. The Japanese frequently cast small slabs weighing in the neighborhood of 50 lb. each, which are very expensive to handle and sample, when considered on the ton basis.

Of late years, the question of moisture in blister copper has been given considerable attention. When a slab is cast, there are numerous cavities in the interior, due to the gases. These cavities are connected with the surface of the slab by capillary tubes, and if a slab is cooled by dumping it into a bosh, considerable water may be

drawn into the cavities. It is not unusual to find slabs containing as much as 0.2 per cent moisture, and this question is the cause of much controversy between the smelter and the refiner as to what allowance should be made to cover this moisture (see page 83, Vol. I, "Principles and Processes").

In all smelting processes, more or less flue dust is produced. The roasting furnaces are the chief offenders in this respect, though they are closely followed by the blast furnaces. The reverberatories, having a relatively quiet atmosphere, do not produce much dust, while that produced by the converters is largely in the form of fume from the volatile metalloids. The collection and re-treatment of flue dust is a considerable item in the cost of operation, and every possible means is utilized to keep its formation down to the lowest point consistent with economical operation. The recovery of flue dust may be accomplished by one or more of the following methods: passing the gases through large dust chambers, in which the velocity of the gases is so reduced that all but the finest particles of dust are settled out. The gases may be filtered through woolen bags after being previously cooled to the proper temperature; this is an expensive method and requires a heavy investment in flues and baghouse. The gases may be passed through a Cottrell electrostatic precipitator in which the solid particles are thrown out of the gas stream by the action of a high-tension electrostatic field. In the Roesing system, the gases flow through dust chambers in which are suspended wires or baffles, and the dust particles impinging upon these adhere, and when sufficient has accumulated the gases are diverted into another chamber and the wires or plates are then shaken to dislodge the dust particles.

The treatment of recovered flue dust consists in briquetting and smelting in the blast furnace, a method formerly widely used but now falling into disuse; agglomerating in rotary kilns, or Dwight-Lloyd sintering machines, and smelting in the blast furnace; or in direct smelting in the reverberatory furnace—the most economical method.

Metal loss is a very important item in the smelting cost, and one that is watched and studied very carefully so that it may be reduced to a minimum. The three chief sources are dust losses in handling, metal contents of slags, and dust and fume losses through the stacks. These losses are a matter of more importance to the custom smelter than to the company owning its own mines, as in the latter case the loss is merely that of the cost of the metal to the point of loss and the potential profit, whereas in the custom smelter the miner has been paid for the contents of his ore and losses represent the loss of actual profits.

The Refining of Blister Copper.—The blister copper produced in the smelting process contains so much impurity that it is unfit for commercial consumption without refining. The following table shows the composition of various grades of blister copper produced at various smelters:

Cu %	Ag oz. p.t.	Au oz. p.t.	As %	Sb %	Pb %	Ni %	Zn %	Fe %	S %
98.8	4.50	0.01	0.004	0.002	0.018	0.41	0.016	0.15	0.10
99.5	2.50	0.02	0.035	0.015	0.001	0.04	0.002	0.03	0.06
98.8	30.25	0.31	0.10	0.040	0.150	0.050	0.120	0.25	0.17
98.4	111.9	0.295	0.02	0.178	0.001	0.005	0.003	0.13	0.20
99.10	73.3	2.09	0.01	0.01	0.048	0.005	0.036	0.056	0.25

In earlier days the refining of blister copper was performed entirely in reverberatory furnaces, but this has been entirely supplanted by the electrolytic process. Of

the former process, it is sufficient to state that it was based on the fact that when copper sulphide and copper oxide were melted together the resulting reaction formed metallic copper, the sulphur passing off in the waste gases as sulphur dioxide. Silver and gold were recovered to a considerable extent by first having a small copper fall in the matte which served as a collector for these metals together with much of the impurities present. The enriched portion was worked up separately, while the purified white metal was carried along to pure metallic copper.

The modern process of refining may be considered to be divided into the following steps: (1) A preliminary fire refining, to remove as much as possible of the impurities, followed by the casting of the copper into anodes. (2) The electrolytic process, consisting in dissolving the anode by means of the electric current and depositing the pure copper on the cathode. In this step the remaining impurities are removed, and any silver and gold contained in the anode are collected as a mud or slime to be recovered by a subsequent treatment. (3) A final furnace treatment of the cathodes, which are not in a form suitable for general commercial use, in order that they may be converted into the proper physical shape for the consumer.

Furnace Refining.—As the methods of operation of the anode and cathode furnaces are almost identical, one description will suffice for both. The furnace treatment is based upon the relatively weak affinity between copper and oxygen, as compared with the affinity between oxygen and the impurities in the copper. The process, therefore, consists in an oxidizing fusion in order to volatilize some of the impurities and to oxidize the remainder, using copper in the form of oxide as a scorifying agent. This being done, the impurities will either pass off in the furnace gases or else float on the surface of the bath as a slag which may be skimmed off.

As the remaining copper is now saturated with oxygen, the next step is to reduce the cuprous oxide to copper by means of some satisfactory reducing medium, after which the copper is cast into the necessary shapes.

In the anode furnace the blister copper should be refined to the highest degree that is economically possible in order to have a uniform high-grade product to send to the electrolytic process. This is necessary, as the success of the latter is largely governed by having uniform operating conditions, and it is generally much cheaper to eliminate impurities by a furnace treatment than by electrolytic methods. It is, however, not possible to remove the last traces of the impurities in the furnace. The great bulk is gotten rid of quite easily, but as the amount becomes reduced it becomes increasingly more difficult without slagging off so much of the copper that the treatment of the resulting by-products becomes too expensive. Just where this point is depends upon local conditions and the relative cost of the two processes. There are also some of the impurities that tend to alloy with the copper and are removed with great difficulty.

The reverberatory furnaces in which the refining is conducted are at the present time constructed with capacities of 500,000 to 600,000 lb. per charge. Owing to the weight of metal contained, they are necessarily of much stronger construction than the reverberatory furnaces used in the smelting of ore. The side walls are constructed of silica brick with a thickness of 12 to 18 in., though there is an increasing tendency to use magnesite brick up to a point above the metal line, and then use silica or a good grade of clay brick from that point up to the roof.

The roof is almost invariably made of silica brick 15 to 18 in. in thickness, though attempts have been made to use firebrick or chrome brick. The great advantage of silica brick is its ability to withstand the temperatures obtained without softening and losing its shape. Firebrick softens at a low temperature, particularly when under pressure, while chrome brick absorbs a great deal of metal, and it is difficult to treat the burned-out brick for the recovery of the copper contents.

be 6 to 8 lb. of steam per pound of coal and with oil, 8 to 10 lb. of steam per pound of oil. In a large plant this waste-heat steam amounts to one-third to one-half of the steam used in the plant, so that the economy is obvious.

The dimensions of some refining furnaces are:

GENERAL DIMENSIONS OF SOME REFINING FURNACES¹

	American Smelting & Refining Co.		Raritan Copper Works		U. S. Metals Refining Co.
Length of hearth.....	50 ft.	36 ft.	37 ft. 6 in.	43 ft.	40 ft. 3 in.
Width of hearth.....	14 ft. 7 in.	15 ft.	17 ft.	14 ft. 3 in.	14 ft. 4 in.
Depth of hearth.....	22 in.	14-16 in.	35 in.	28 in.	30 in.
Hearth area, square feet....	665	490	559	553	496
Length of grate.....	9 ft.	Oil fired	Oil fired		8 ft. 3 in.
Width of grate.....	8 ft. 4 in.				7 ft. 4½ in.
Area of grate, square feet...	75				60.8
Height of roof above hearth at bridge.....	6 ft. 4 in.	6 ft. 10 in.	7 ft. 9 in.	7 ft. 6 in.	7 ft. 2 in.
Height of roof above hearth at flue.....	3 ft. 6 in.	3 ft. 6 in.	5 ft. 10 in.	4 ft. 2¾ in.	4 ft. 9 in.
Area of flue, square feet....	12.47	12.00	11.50	9.15	12.75
Tons output per 24 hours...	200	178	250-275	275-325	226

¹"Metallurgy of Copper," Hofman-Hayward.

The various operations of the furnace may be classified as charging, melting, oxidizing, poling, and casting, and will be taken up in their order. The large furnaces are charged by means of electrically operated charging machines which handle up to 6000 lb. of copper at one time and which will charge a 200-ton furnace in less than 2 hr. In the smaller installations the old method of hand charging is still in use. This consists of placing the slabs of copper on a paddle and sliding them into the furnace. This is a slow and expensive method and is rapidly being displaced. Owing to the large amount of space occupied by the slabs, the amount that can be charged at one time is usually less than the capacity of the furnace, and it becomes necessary to recharge a small amount after the original charge has been melted down.

At the plant of the Ontario Refining Co., molten blister copper is conveyed 1¼ miles from the smeltery to the refinery in a specially designed car holding 70 tons of hot metal. This car is spotted alongside the furnace and the contents poured therein through a launder.

When charging cathodes, a larger amount can be charged during the first charging, as they stack better and do not occupy as much space relatively. At the plant of the Nichols Copper Co. a unique method of charging is used, which consists of sliding the cathodes into the furnace by means of a chute. By this arrangement, the furnace is not permitted to cool down, and the fuel consumption is thereby decreased. With the charging crane the doors of the furnace must be opened, and by the time the furnace is charged it has cooled down to a dull red or black heat.

When the charging of the furnace has been completed, the doors are luted up and the fire urged to the utmost extent. As copper is an excellent conductor of heat, the metal rapidly absorbs the heat and soon starts to melt on the edges. During the melting, the flame is kept strongly oxidizing in order to have a sharp cutting heat

and to form as much oxide as possible. When the surface of the bath is smooth, the firing is continued strongly until the metal on the bottom has melted, which is recognized by the charcoal or coke covering of the preceding charge rising to the surface. Between the time when the charge is flat and when the metal is afloat, the slags that form are skimmed. The amount of slag formed depends on the nature of the material charged. Average blister copper will produce about 3 to 4 per cent of its weight of slag, cathodes about 1 to 2 per cent, and fowl coppers may run as high as 30 per cent. With coal firing the ash of the coal is frequently blown over into the bath and forms slag, and with powdered coal there is a considerable increase, at times amounting to 50 per cent. Fuel oil, on the other hand, has no tendency to increase the amount of



FIG. 7.—Application of silica slurry, Clarkdale smeltery, Phelps Dodge Corp.¹

slag formed. As refinery slags are high in copper (30 to 50 per cent), it is seen that the re-treatment charges are heavy, and a small increase in the amount of slag formed is immediately reflected in higher costs.

When the metal in the bath has been skimmed clean, a say ladle, which is a small ladle with a long handle used for taking samples of the molten metal, is dipped into the furnace, and a test button taken to determine the condition of the metal. If, while the button is solidifying, it breaks through the crust and "throws a worm," this is indicative of sulphur, and a green pole is inserted in the bath to agitate the metal and drive out the sulphur held in solution by the copper. During this poling the atmosphere is kept strongly oxidizing. Buttons are taken frequently until the evidences of sulphur have disappeared. This operation is known as poling down. When the sulphur has been poled out, the copper in the bath is oxidized by inserting air pipes through which compressed air is forced. This not only itself oxidizes the copper to a considerable extent, but, by the violent agitation it causes, exposes a

¹Figs. 7 and 8 are from R. A. Wagstaff's "Changes and Improvements in Modern Copper Smelting," T.P. 1669, Trans. A.I.M.E., Feb., 1944.

large surface of the molten metal to the oxidizing influence of the hot gases. To assist the oxidizing, a rabble may be introduced through the skimming door and by means of a chain suspension swung back and forth the surface of the metal broken into thin sheets or sprays. It is found that the rabble is more effective as a means of oxidizing than the air jets, but, owing to the great mass of copper to be oxidized and the hot and fatiguing work of swinging the rabble, its use as the sole means of oxidizing is impracticable.

During this period of blowing and flapping, buttons are taken to show the progress of the oxidation. As the amount of cuprous oxide in the bath increases, the surface of the button sinks and the fracture shows a color approaching a brick red. When the metal is saturated with oxide, there will be a deep depression, the fracture will show a bubble in the center, and the fracture will be coarsely cubical and a strong brick-red color. During this period, more or less slag will form and will be skimmed off, so that the surface of the metal will be kept clean for the action of the hot oxygen in the gases. The cuprous oxide formed acts as a scorifying agent and is the effective means of removing the impurities in the metal.

When the buttons show that the charge is saturated with oxygen or "set," the air pipes and rables are removed and the surface of the bath is covered with coke or charcoal. The doors are closed and tightly luted up so as to prevent the admission of excess air. A pole is then inserted in the bath in order to reduce the cuprous oxide to metallic copper.

The poles used for this operation are usually hardwood, but softwood is readily usable, the chief objection being the heat developed at the poling door, with the attendant discomfort to the men, and more wood is required per ton of copper. An average amount of wood for poling may be considered to be 100 to 150 lb. per ton of copper. If wood is used to make the charcoal covering for the bath, the amount is increased to 250 lb. per ton. As the pole burns away, it is pushed further into the furnace, and when it becomes too short to hold by the chain block, it is pushed into the furnace and becomes a brand, while a new pole is introduced.

During this time, test buttons are taken and the surface and fracture observed. The fracture gradually changes from coarsely cubical to finely granular, then fibrous, the color changing from a brick red to a salmon pink. When the poling is finished, the surface of the button is slightly rounded, and the fracture is silky and of a rose color. The copper is now said to be "tough pitch" and is ready for casting.

During the progress of the refining the various impurities behave about as follows: Iron and cobalt oxidize and slag off readily, though if cobalt is present in any considerable quantity a considerable time may be required for its complete elimination.

Nickel is a very difficult element to slag on account of its strong affinity for copper. With high-nickel coppers the first few percentages of nickel readily pass into the slag, but as the amount decreases the slagging becomes slower and slower. To eliminate the last portions is extremely difficult. The bath must be skimmed clean, and, by continuing the oxidation, the nickel oxide forms as a powder and may be skimmed off. If, however, there is any reducing action in the furnace, the nickel easily reduces and is absorbed by the copper.

Sulphur requires a great deal of poling and oxidizing to effect its removal, and if present in blister copper to any considerable extent will make the furnace work very hot. If an excessive amount is present, there will result a great deal of trouble from the formation of matte on the surface of the bath.

Lead partly volatilizes and is partly slagged. With considerable lead present it may become necessary to throw the charge coarse with a small addition of matte and reoxidize. When present in any considerable quantity, lead will vigorously attack silica bottoms as soon as any oxide is present, and it may become necessary to use

magnesite brick bottoms when handling blister high in this element. Zinc is readily oxidized, and its elimination is simply a question of time of blowing.

Arsenic and antimony partly volatilize, but are eliminated with considerable difficulty. In some cases it becomes necessary to treat the bath with a flux of lime and soda in order appreciably to reduce the amounts of these undesirable elements. In severe cases it is necessary to give the copper a second refining.¹

When the metal is finally ready for casting, that from the fire refining of blister copper is cast into anodes for the electrolytic process. For the multiple system these are slabs 24 × 36 in. or 36 × 36 in. and about 2 to 3 in. in thickness. When used

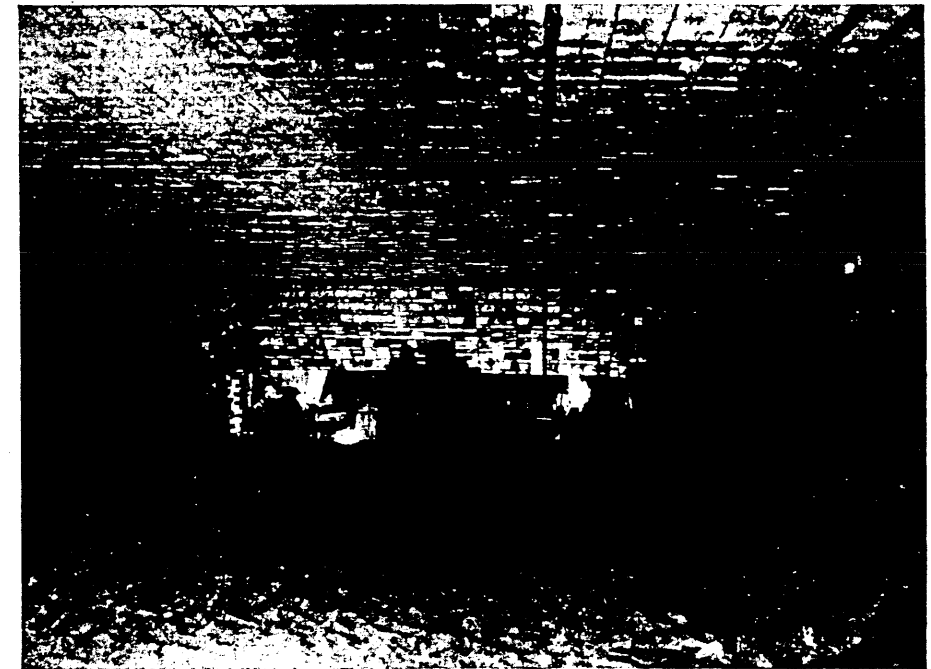


FIG. 8.—Suspended arch in reverberatory furnace, Hudson Bay Mining & Smelting Co.

for the series system, the anode may be cast as a slab for rolling, or as a long thin anode for direct dissolving.

When the anode is to be used direct, lugs are cast so that it may be easily supported from the conductor bar or hanger bar. In some cases, loops of heavy copper wire are placed in the mold and the metal cast around them. A heavy copper bar is passed through the loops and is used to make the contact.

When small furnaces are in use, the copper is frequently cast by hand ladling, but with the increased size of the furnaces it becomes necessary to find some faster method. It is now the universal practice with large furnaces to draw off the metal from the side or end of the furnace through a tapping slot. This slot or taphole is filled with a mixture of clay sand and a small amount of coal, hard enough to withstand the pressure of the metal on the interior of the furnace, but soft enough to permit of cutting a gutter for the flow of the metal. This plug is held in place during the working of the furnace by transverse iron bars, about 1 in. square, placed on top of one another

¹ For researches on relative slaggability, see *Mineral Ind.*, p. 248, 1901.

and held by guides fastened to the side plates of the furnace. These bars are removed at the time of casting, and the clay plug is cut away from the top sufficiently to permit the copper to flow over the edge into a launder leading to the ladle. As the level of the copper in the furnace falls, the clay plug is cut down more and more. If at any time it is desired to stop the flow of metal, a ball of clay is placed in the taphole and pressed down with a stick.

In the new Phelps Dodge plant at Morenci, the anode furnaces are of the tilting type, 13 × 25 ft., holding about 175 tons. They are set at a height sufficient to permit complete emptying into the pouring spoon. Complete rotation is possible, and gears, riding rings, cradles, and drive are interchangeable with similar parts of the converters. The lining is 18 in. of magnesite brick in the lower half and 13 in. magnesite in the upper half, backed up by insulating brick to reduce heat loss. The low-pressure gas burner is mounted on a hinge to permit swinging away from the port. Only a short movable flue is provided, without a stack, to avoid undesirable draft.

There are several types of casting machines for the casting of anodes. The Walker wheel has the molds on the circumference of a wheel approximately 21 ft. in diameter. The wheel is turned by hydraulic or electric power, and the molds are brought under the furnace ladle where they are stopped while the mold is filling. The wheel is then revolved until the next mold is under the ladle. When the newly cast anode is about three molds away from the ladle, it is sprayed with water to cool the metal, and at the same time the mold is cooled by a spray from underneath. When the anode is nearly opposite the ladle, it is lifted from the mold by means of a push pin which passes through the mold and slides on an inclined track. The anode is then lifted from the mold by a crane and placed in a bosh filled with running water in order to cool to the room temperature.

The straight-line casting machine consists of a series of molds carried by an endless belt in front of the ladle. When a mold is filled, it passes toward a bosh, being sprayed on its journey, and at the end of the belt where the molds pass underneath, the anode is either dumped into the bosh or else lifted out of the mold by a crane and placed in the bosh for cooling.

In hand lading, the ladle man stands in the center of a wheel somewhat similar in shape to the Walker wheel, and, as each mold passes, it is filled with copper and passes around to the rear, where it is cooled and removed either by a hoist or by a man using a long-handled lifter.

Anode molds are generally made of copper, though in some instances cast-iron molds are used. The advantage of copper lies in the fact that when the mold has outlived its usefulness it can be charged into the furnace and the copper recovered and sold at market value, while a cast-iron mold has only a low scrap value. In order to prevent the copper from sticking to the molds, they are washed with pulverized silica, which is applied at such a point that the heat of the mold will dry it out before the ladle is again reached.

The furnace refining of blister copper should be carried to the highest possible point in order to produce the best results in the electrolytic refining. A well-refined anode will dissolve readily and evenly and will give a good deposit, while an improperly refined anode will dissolve unevenly and give rough deposits and a heavy percentage of scrap which has to be re-treated. It has been very clearly demonstrated that any extra expense incurred in the anode refining to ensure a high-grade product will result in a much greater saving in the balance of the refining process.

The electrolytic refining of copper is based on the selective action of the electric current in the following manner. If two metal plates are suspended in an electrolyte, and a direct current is passed from one plate to the other, the metal of the plate where the current enters, known as the anode, will be dissolved, provided the composition

of the electrolyte is of the proper type. The plate at which the current leaves is known as the cathode, and what happens at this point depends on the nature of the dissolved metal and the composition of the electrolyte. The constituents of the

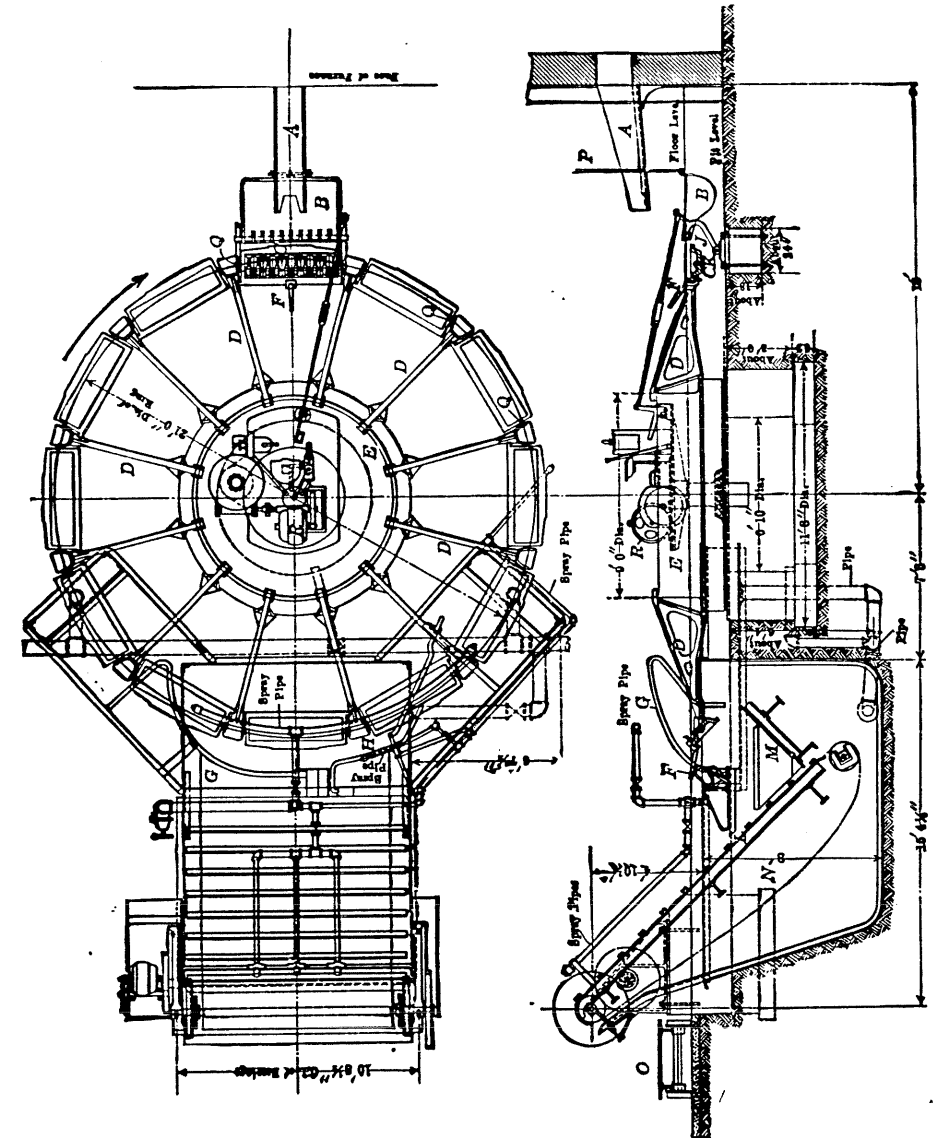


FIG. 9.—Walker casting machine.

electrolyte are partly ionized, and the individual ions have definite discharge potentials depending upon their positions in the e.m.f. series (see page 378). Those ions having the lowest discharge potential will be discharged as long as they exist in sufficient amounts to carry the current. If there is an insufficient amount, the ion next highest will be discharged. In an aqueous electrolyte the hydrogen ion is present

and will be discharged unless there is present some other ion standing below it in the series. Copper is in this position and, therefore, will be discharged before hydrogen. The electrolytic refining of copper is, therefore, based upon the fact that, if a copper anode is suspended in an electrolyte composed of copper sulphate and sulphuric acid, it will be dissolved and the copper pass into solution. At the cathode, which is also copper, the copper in solution will be deposited while the hydrogen present will be unaffected.

The impurities associated with the copper in the anode do not deposit on the cathode because they stand higher in the e.m.f. series than either copper or hydrogen and, therefore, while they dissolve in the electrolyte, remain in solution, or else the composition of the electrolyte is so adjusted that they remain on the anode as insoluble alloys or compounds.

The impurities that, as a rule, pass into solution and remain there are Fe, Ni, Co, Zn, As, and Sb. Those that are insoluble and remain on the anode as a slime are Ag, Au, Pt, the rare metals, and Se, Te, and Pb.

Where an impurity exists in the anode as a chemical compound it will tend to pass into the slime, as chemical compounds have a much lower electrical conductivity than the copper, and these compounds largely segregate in the anode. The purer metal immediately surrounding them is dissolved, allowing the compound to fall into the slime, where it may lie inert or else be slowly attacked by the electrolyte and pass into solution. Those elements which alloy with copper may either dissolve or pass into the slime, depending upon their nature and properties.

Two systems of electrolytic copper refining are in use at the present time, the multiple and the series, differing in the arrangement of the electrodes.

The Multiple System.—In the multiple system, the anodes and the cathodes are connected in multiple and are suspended crosswise in a lead-lined tank. The anodes are generally 2 × 3 ft. or 3 × 3 ft. in area and 2 to 2½ in. thick, weighing 400 to 600 lb. The number of anodes varies from 26 to 32 per tank, and they are given a spacing of about 4 in.

The multiple cathodes consist of pure copper starting sheets suspended between the anodes. The preparation of the starting sheets is an expensive operation, requiring skilled labor. In the manufacture of the starting sheets, anodes of the purest grade of copper are used, and the anode is wider than the regular anodes to ensure the edges of the starting sheet being perfect. The starting sheet is made by depositing copper on a rolled and stretched copper blank, which is coated with a mixture of graphite and oil, or else gasoline and oil, or other mixture that has been found to be satisfactory for the purpose. This coating is for the purpose of allowing the sheet to be readily stripped from the blank. To prevent copper being deposited on the edges of the blank, these are protected by covering them with grooved strips of wood, which are removed when the sheet is stripped from the blank, or else the edges of the blank are painted with a heavy asphalt paint, and a shallow groove is cut in the blank at the point where it is desired to have the sheet break off.

The process of manufacture of the starting sheet consists in first giving the blank a coating of the oil paint; the edges are then painted with asphalt or the wooden strips put in place, and the blank is hung in the tank while the current is on, and allowed to remain for the necessary time, usually 24 hr. The blanks are then drawn from the tank one at a time. The operator strips the thin sheet from the blank with a sharp-edged knife, one sheet from each side, repaints it, and it is returned to the tank. The thickness of the sheet is usually about ¼ in., and a 3 × 3-ft. sheet will weigh about 10 lb. It is of the greatest importance that the current be flowing when the blank is placed in the tank, or else the oil will be washed off by the hot electrolyte and the new deposit will be burned fast to the blank when the current is turned on. In

order to hang the starting sheets in the regular depositing tanks, two loops are fastened to each sheet. These loops are made of starting sheets which are cut into the proper-size strips and are fastened to the sheet by punching and bending back the sharp corners of the punched portion.

As the starting sheets must have good tensile strength, they are usually made at a current density lower than that used in the regular tanks, and the electrolyte used is kept very pure. The number of tanks required for this work will depend upon the number of cathodes to be drawn daily from the regular tanks, as a starting sheet must be produced for each cathode drawn.

The tanks used for the multiple system are made of wood or reinforced concrete, the latter being preferred in recent installations. All tanks are lined with 6 per cent antimonial lead to protect the wood or concrete from attack by the electrolyte. The dimensions of a tank for 30 anodes with a surface of 3 × 3 ft. is approximately 11 ft. long by 3½ ft. wide by 3½ ft. deep. Several arrangements of tanks are in use at the present time, the earlier arrangement being two tanks side by side and in rows depending upon the size of the tank room. As this arrangement required a large amount of copper to be tied up in bus bars, the Walker arrangement was developed, in which there are but two rows of tanks, but there are 15 to 20 tanks, having a common partition, in each row. As the electrodes of one tank are connected to the electrodes of the adjoining tank by the use of a light triangular bar to which the cathodes of one tank and the anodes of the next tank are connected, there is a great saving in copper. This arrangement is at present the most widely used.

The tanks are built on masonry piers high enough to permit of proper inspection underneath for leaks, etc. At the top of the piers are glass blocks having a thin sheet of lead placed on the top. The glass block serves as an insulator; the lead sheet protects the glass from any drip from a leaky tank. The tanks rest on longitudinal sills 8 × 8 in., which rest upon the top of the piers. There are many variations in the constructional details of the tanks, each refinery having its own ideas on the subject.

The electrical connections depend on the tank arrangements. In the older system where two adjacent tanks are arranged in cascade of 8 to 10, the current is led to each pair of tanks by a heavy copper bus bar. The current leaving the cathode bar was conducted to the adjacent tank by means of a heavy copper connection plate upon which the anode bar rested. The current then left this tank through a heavy bus bar which led it to the next pair of tanks in the cascade. In the Walker system the current is led to the first tank by a heavy bus bar. The common partition between the tanks supported a light triangle bar upon which the cathode bars of the preceding tank and the anode bars or lugs of the succeeding tank rest. At the end of the row of tanks the current was carried by a heavy bus bar to the next row of tanks. There is thus a great saving in the amount of copper tied up in conductors when using the Walker system.

In the multiple system, as the electrodes are in multiple, each anode must have its individual current supply. With a depositing surface of 540 sq. ft. and a current density of 20 amp. per sq. ft., the total current required will be 540 × 20, or 10,800 amp. per tank. With 30 anodes per tank, each anode will require 360 amp. The use of such large currents requires conductors of large cross section to prevent overheating and consequent loss of power, and this constitutes a large proportion of the initial investment in a multiple tankroom. The generation of currents of this magnitude also requires expensive generating equipment in the powerhouse.

The operation of the multiple system is about as follows: The anodes, having been straightened, are placed in the tank by an overhead crane and are then evenly spaced by the tankmen. The starting sheets are straightened and a copper bar passed

through the loop. They are then hung in the tanks and the loops securely clamped to the cathode bar by tongs specially designed for this purpose. This is done to ensure a minimum contact resistance between the loop and the rod. The starting sheet is then accurately spaced between the anodes. All anode and cathode contacts with the bus bars or triangle bars are then given a coating of oil in order to prevent acid and salts from creeping in and spoiling the contact. The tank is then filled with electrolyte and the current turned on. At the end of 48 hr. it is customary to withdraw the cathodes one by one and straighten them, as the initial deposit has a tendency to make them curl slightly.

The time required for making a full-weight cathode depends upon the current density used, the quality of the anode, and various factors peculiar to the plant in question; but usually two cathodes are produced from each anode, and the time required per cathode is 10 to 14 days. During this time the tanks are gone over daily and inspected for short circuits, and when these are found the cathode is lifted up and the nodule causing the short circuit broken off, or else it may be removed by the tankman's sweeping a copper rod across the face of the cathode.

When the first crop of cathodes has run its full time, the tanks are cut out of circuit by short-circuiting the entire section of tanks to be drawn by the use of a heavy copper cutout. The cathodes are removed by an overhead crane and taken to a wash box, where they are thoroughly washed by a spray of hot water to remove any adhering slime and electrolyte. They are then piled on a car and sent to the wire-bar furnace.

The anode mud that contains the silver and gold is then swept from the face of the anode by means of brushes with long handles, or else the anode may be withdrawn from the tank and taken to a wash box, where the slime is washed off by hot water and the anode returned to the tank. A new set of starting sheets is placed in the tank, the contacts gone over as before, and the current turned on. During this second run of cathodes, the anodes are carefully watched to see when they become too thin for proper working. When an anode gets scrappy, due to its being thinner than it should be, or else having dissolved at a faster rate than its mates, it is withdrawn from the tank and replaced by a piece of heavy scrap, a supply of which is kept on hand in the tankroom for such purposes.

At the end of the run the tank is cut out of circuit as before, the cathodes removed, washed, and shipped, and the scrap anodes drawn from the tank by the crane and thoroughly washed to remove all adhering slime. They are then sent back to the anode furnace for remelting. Any heavy scrap is generally kept in the tankroom for the purpose, described above, of replacing anodes that have gone scrappy, before their time.

The electrolyte is pumped out of the tanks, a plug in the bottom of each tank is removed, and the accumulated slime is flushed into a launder, which conveys it to a slime tank, where it is screened to remove coarse pieces of metallic copper and is then pumped to the silver refinery for the recovery of the precious metals contained.

The tank is thoroughly cleaned of all adhering salts and slimes, any leaks that may have developed are repaired by the lead burners, the triangle rods are cleaned of salts and dirt, and the tank is then ready for another run.

The amount of scrap made in the multiple system will depend on the character of the anode, the current density, and the care taken in casting the anodes uniformly thick. The usual practice will make about 15 to 20 per cent scrap, a large part of which is accounted for by the lugs that are undissolved. The percentage of scrap made is kept as low as possible on account of the re-treatment cost, the tie-up in metals, and the delay to putting in process contract material.

The Series System.—In the series system the electrodes are connected in series and the same current serves each electrode. There are no starting sheets as the back of each anode serves as the cathode for the preceding anode.

There are two modifications of the series system: In one a rolled anode is used, in the other a cast anode is used. The first is in operation at the plant of the Baltimore Copper Co., the second at the plant of the Nichols Copper Co.

At the Baltimore plant the anode material must be of good quality to permit of rolling without cracking. The anode furnaces cast a slab, which, while red hot, passes through the rolls and is rolled down to a thickness of about 14 in. It is then cut into plates approximately 11 × 24 in., which are straightened and two plates placed in wooden frames, which are placed in the tank. The tanks are 11 ft. 6 in. in length, 25 in. in width, and have a depth of 26 in.; 135 electrodes are placed in each tank.

The current enters the tank through the first electrodes, passes through all the electrodes in series, and leaves through the last electrode, which is a copper plate. The electrodes act as both anodes and cathodes, the side receiving the current being the cathode, and the side from which the current leaves being the anode. As a result, the impure metal of the anode is dissolved from one side of the plate while pure copper is deposited on the other side of the plate to approximately the same thickness.

The deposition is finished when the anode has been dissolved to the desired degree, which is usually a complete dissolving, so that there is little or no scrap, other than that from the rolling and the cutting of the plates and that left in the grooves of the strips. The cathodes are removed from the tank, washed, and sent to the wire-bar furnace. The slime remaining at the bottom of the tank is removed by hand and the tank is carefully cleaned out before the next run.

At the Nichols plant the anodes are cast, and average 12 × 54 × 5/8 in. They are straightened, and the cathode side is painted with a mixture that will permit of readily stripping the cathode from the undissolved portion of the anode. The anodes are then hung on an iron bar, there being five anodes to a bar, and 121 bars are hung in a tank. The tank is then filled with electrolyte and the current turned on. When the deposition has proceeded to a point where the amount of anode remaining is about 8 per cent, the deposition is considered finished; the electrodes are removed from the tank by a crane and carried to the stripping room, where the remaining anode scrap is removed and sent back to the anode furnace for re-treatment, the cathodes being sent to the wire-bar furnace, and the slime flushed out and sent to the silver refinery.

The current density used in the series system is the same as that used in the multiple system, but as the electrodes are in series the amount of current per tank is much less. Where a multiple tank having a depositing surface of 540 sq. ft. requires a current of 10,800 amp., a series tank having a depositing surface per plate of 4 sq. ft., as at Baltimore, or 23 sq. ft., as at Nichols, will require 80 or 460 amp., respectively. These small currents avoid the use of conductor bars of large cross section, and, as there are but few contacts per tank in the series system as against approximately 120 in the multiple system, the contact losses are reduced to a minimum.

The voltage across the electrodes in the series system at the solution level is approximately the same as that in the multiple, for equal spacing, so that, while the multiple system has a low voltage per tank, the series system, which in reality consists, electrochemically, of a number of multiple tanks in series, has a voltage corresponding to the number of electrodes in series. Where the multiple system has a voltage at the solution level of, say, 0.2 volt, the series tank, with 135 electrodes, will have a voltage of 27.0 volts, and with 121 electrodes the voltage will be 24 volts, if the electrode spacing is the same in all cases. The electrode spacing in the series system, however, is closer than in the multiple system, and the voltage is correspondingly reduced.

The over-all voltage per electrode in the series system is much less than in the multiple, therefore, both on account of the closer spacing and the almost complete absence of contact resistances. The average voltage may be taken as about 20 volts per tank at a current density of 20 amp. per sq. ft.

This high voltage makes it necessary to use tanks having an insulating lining, and the lead-lined tanks used in the multiple system are not practicable. The usual construction is either of wood lined with some asphalt compound, slate, or else concrete lined with asphalt, the last being preferable, due to a longer life and cheaper maintenance.

The multiple and series systems may be roughly compared as follows: The multiple system casts heavy, thick anodes; the series requires rolled or light thin cast anodes. The multiple system requires the preparation of a special starting sheet, which is an expensive operation requiring skilled labor. The series system uses no starting sheet, but it is necessary to strip off the backs, an operation performed by common labor. The multiple system requires heavy currents per tank, necessitating heavy conductor bars with a consequent large tie-up of copper. The series system uses low currents and avoids the use of heavy conductors.

The copper produced per kilowatt-day in the multiple system at a density of 18 amp. will average about 165 to 180 lb. In the series system the production per kilowatt-day will average about 340 to 380 lb. The power requirements in the series system are thus about half those in the multiple system. The efficiency in the multiple system will average about 90 per cent, in the series system about 70 per cent, due to the current leaking past the plates. The scrap produced in the series system is less than that produced in the multiple system with a consequent less cost for re-treatment. The greater output per tank in the series system requires less tanks for any given output. The tanks used in the series system must be lined with insulating material. In the multiple system, lead linings are used. The metal losses in both systems are about equal, while the copper, silver, and gold locked up in process are less in the series than in the multiple.

Outside of the shape and arrangements of the electrodes and the tanks, the other features of electrolytic refining are common to both processes. The electrolyte has a composition of approximately 35 g. per l. copper, 140 to 200 g. per l. sulphuric acid, together with small amounts of such impurities as iron, nickel, arsenic, and antimony as may accumulate from the dissolution of the anode. The electrolyte has a marked negative temperature coefficient and, therefore, is heated by steam to increase its temperature and reduce the electrical resistance. The degree of heating used depends upon the relative cost of power and steam as well as the electrolyte composition, to a certain extent. The usual temperature is about 130°F. As the power used in overcoming the resistance of the electrolyte appears therein as heat, there is considerable heating from this source. The amount of steam used in the multiple system per tank will be greater for the same temperature than in the series system, owing to the different amounts of power developed in the tanks. A multiple tank will develop approximately 3 kw., while a series tank will develop about 10 kw.

Owing the tendency of the electrolyte to segregate under the action of the current, it becomes necessary to circulate it through the tanks. The segregation is more marked in the case of high-current densities than in low densities. It is caused by the fact that at the face of the anode, where copper is passing into solution, the electrolyte consists largely of copper sulphate of high specific gravity and there is a tendency to stream downward. At the face of the cathode, where copper is removed from the electrolyte, the latter becomes largely sulphuric acid of lighter specific gravity and the tendency is to stream upward. If, therefore, there were no circu-

lation at all, the electrolyte would soon form two distinct layers, that on top being high in acid and low in copper, while the bottom layer would be high in copper and low in acid. As a result, the deposition would be largely confined to the lower part of the cathode, while there would be a copious evolution of hydrogen at the top of the cathode accompanied by spongy copper. The efficiency would, therefore, be greatly decreased, and the power per ton of copper increased. With an adequate circulation this tendency is counteracted to a large extent and the deposit kept regular. The higher the current density, the greater will be the amount of circulation required to prevent stratification. On the other hand, an increased circulation tends to keep the slime in the tank stirred up, resulting in increased metal losses. The choice, therefore, lies between greater efficiency of deposition and increased metal losses. The normal rate of circulation will be about 3 to 4 gal. per min. for current densities of 15 to 20 amp.

At some plants the electrolyte is admitted at the top of the tank and withdrawn from the bottom, while at others the flow enters at the bottom and is withdrawn at the top. The latter requires less solution, and there is less danger of a tank being flooded. This is because the solution on cooling becomes denser, and, therefore, a greater head of the hot entering solution is required to force the cooler solution from the bottom of the tank; and in case the current has been off for some time, so that the solution has become quite cool, the head required to raise the cold column of solution in the outlet pipe may be such that it is more than the tank will hold. On the other hand, the objection to the top overflow is that this type of circulation opposes the natural settling of the slime. As, however, the rate of flow per square foot of cathode surface is exceedingly small, this objection appears to be more theoretical than actual.

The older plants had their tanks arranged so that the electrolyte flowed through as many as six tanks in cascade. This practice reduced the amount of electrolyte required, but the great cooling that occurred so increased the resistance that the loss in power more than offset the reduction in the tie-up of metal in solution. The modern practice is, therefore, to reduce the number of tanks in cascade to one or two, thus preventing severe temperature inequalities and giving better efficiency and power consumption.

Circuit Resistance.—The current used in the electrolytic refining is, of course, direct current, and the amount carried by the bus bars will vary from 10,000 to 12,000 amp. for the multiple system to 500 in the series system. As the output depends upon the current, while the power depends upon the resistance, and the problem in electrolytic refining is to obtain the greatest output per unit of power, the question of resistances must be given very careful attention. The following resistances are encountered in the various systems:

Multiple.—Bus bars, bus-bar joints, anode contacts, anode, electrolyte, cathode, cathode loops, cathode-loop contacts, cathode rods, cathode-rod contacts, and other small resistances, such as resistance of the slime layer on the anode, transfer resistance, counter e.m.f., etc. The magnitude of these resistances is approximately as follows: contacts, 15 per cent; electrolyte, 60 per cent; conductors, 15 per cent; counter e.m.f., 5 per cent; slimes, etc., 5 per cent. In the series system there are the following resistances: bus bars, anode rod, anode hangers, anode, electrolyte, cathode, cathode hangers, cathode rod, and also the other small resistances mentioned in connection with the multiple system. The magnitude of the above is approximately as follows: contacts, 2½ per cent; electrolyte, 85 per cent; conductors, 2½ per cent; counter e.m.f., 5 per cent; slimes, 5 per cent. As the cost of power is one of the chief items in the refining of copper, constant thought is given to means whereby these resistances may be reduced and power saved.

Some of the ways in which savings may be made are as follows:

Conductors.—As the resistance of any conductor varies as its cross section, it is evident that any increase will result in decreased resistance. An increase in cross section, however, will increase the weight and, therefore, the cost of the conductor. Thompson's rule that the most economical cross section is that for which the interest on the investment equals the cost of power lost is applicable in this case, particularly for bus bars. For the other conductors in the tank, conditions prevent its application. Thus the anode lugs must be of sufficient strength to support the weight of the anode, and hence are usually of far greater cross section than required for the current. As the cathode loops are made of thin copper strips, these are generally of insufficient cross section and hence carry a current density greatly in excess of that which is most economical.

Contacts.—The reduction of this resistance calls for two things: (1) ample area of the contact surfaces, (2) the elimination of as many contacts as possible. This resistance is one of the largest in the tankroom, outside of that of the electrolyte, and much ingenuity has been shown in reducing it. Formerly, anodes were suspended by two hooks, giving five contacts, two at each hook, and one at the contact of the anode bar with the bus bar. The modern anode has but one contact, due to cast lugs being used which make the contact with the bus bar. Cathodes were formerly suspended by hooks which have been replaced with firmly attached loops, the attachment being below the surface of the solution, where they soon become covered with the deposit and become an integral part of the cathode. An attempt has been made to eliminate the contact between the cathode rod and the triangle rod by having the cathode rod rest directly upon the anode lug in the adjacent tank.

One of the best methods of keeping contact losses at a minimum is to keep them clean. As there is generally considerable heat generated at any contact, any solution that may be splashed thereon will soon be converted into anhydrous sulphates, which prevent an effective contact. The most effective way so far developed for the prevention of this formation is to apply a thin coating of oil to the contact surfaces. This will keep them clean for a long time and costs little to apply.

While the numerical value of each contact loss appears to be so small as to be almost insignificant, it must be remembered that there are a great many of these contacts throughout the tankroom and their cumulative effect is sufficiently large to amount to a considerable waste of power.

Electrolyte.—The resistance of the electrolyte is affected by its temperature and composition. The temperature coefficient is negative, so that an increase in temperature decreases the resistance. The higher it is possible to carry the temperature, the lower will be the resistance. There is, however, a practical limitation to the degree of heating on account of the cost of the steam exceeding the saving in power beyond a certain point, depending upon local conditions. Too high a temperature may also affect the character of the deposit, and the higher the temperature, the greater the amount of evaporation and the higher the humidity in the tankroom with its attendant discomforts.

The composition of the electrolyte has a great effect on its resistance. As the conductivity is dependent on the presence of hydrogen ions, an increase in the content of acid will increase the number of hydrogen ions present and decrease the electrolyte resistance. The presence of sulphates increases the resistance. These sulphates are not only the copper sulphate composing the original solution, but also the accumulated sulphates from the impurities in the anode, such as iron, nickel, and zinc. To secure an electrolyte of minimum resistance, it is necessary to keep the free acid as high as possible and the sulphates as low as possible. The practicable limits to high acid and low sulphates are that there must be a sufficient amount of copper in the

vicinity of the cathode so that only copper ions will be discharged. This limitation, therefore, requires the copper to be kept not lower than 30 g. per l. in average work. If the acid is too high the saturation point of the sulphates present becomes very close to the operating temperature of the solution, and any cooling that may occur is likely to cause a salting out of these sulphates on the cathode, giving a very rough and contaminated deposit. The lower the contained sulphates in the solution, the higher can the acid be maintained.

Counter E.m.f.—The cause of the counter e.m.f. is largely due to the formation of concentration cells at the electrodes due to differences in the composition of the electrolyte. This may be overcome to a certain extent by increasing the rate of circulation of the electrolyte, but there is a very practical limit to this on account of the danger of stirring up the anode slime and contaminating the cathode, thereby increasing the precious metal losses and producing impure copper.

The formation of concentration cells at the surface of the cathode also causes the copper content of the electrolyte to increase, owing to the fact that, if at the top of the cathode there is a solution containing higher acid and lower copper than contained by the solution at the bottom of the cathode, a concentrate cell will be set up and copper will tend to pass into solution at the top of the cathode and be deposited at the bottom of the cathode. But as the efficiency of deposition is less than that of dissolution the copper in the solution will increase, and this amount of increase will be greater the greater the difference in solution composition.

Slimes.—The resistance of the slime adhering to the surface of the anode will depend largely on the purity of the anode. A high-grade anode produces slime that has low electrical resistance, while an impure anode gives a slime that may have a very high resistance, and should the nature of the slime be such that it covers the anode with a very heavy, dense layer, the anode may be made almost insoluble with a correspondingly great increase in the voltage necessary for the operation of the tank.

Current Density.—The current density to be used in electrolytic refining depends upon a number of factors. It is of great importance, as the design of the tankroom depends upon it. The two main factors affecting the selection of current density are the cost of power and the average composition of the anode. As the power cost varies directly as the square of the current density, a point is soon reached where the power cost becomes prohibitive. When the anode contains a large amount of silver and gold, a high current density will tend to give high metal losses in the cathode, due to the necessity of maintaining a high rate of solution circulation.

A high current density generally increases the labor cost because the weight of the cathode is more or less fixed by the physical labor of handling, and a high current density means pulling cathodes of younger age. This more frequent pulling also requires the use of a larger number of starting sheets, the preparation of which is an expensive item. The question of interest on metals locked up in process plays a very important part in the determination of current density. If the anodes are high in silver and gold, the saving due to getting these metals on the market earlier will often pay for an otherwise uneconomical current density.

Increased current density requires the use of fewer tanks and less building space for a given output. This means a lower initial investment and, where construction costs are high, may have great influence on the question.

The average current density in use at the present time will vary from 15 to 20 amp. per sq. ft. of cathode surface. In many cases this density is too high for present power costs, but as the plants were designed at a time when power was cheaper than at the present, it was correct at that time, and the only way in which the density can be reduced without building additional tanks is to curtail the output, and the loss sustained in so doing may be much greater than the loss due to increased power costs.

Important factors

Current Efficiency.—The term "current efficiency" is an expression of the ratio of the amount of product actually obtained to that theoretically obtainable in accordance with Faraday's law. It is always less than unity on account of various factors, such as current leakage, short circuits in the tanks, and the deposition of hydrogen at the cathode. As the output of the tanks is directly proportional to the current efficiency obtained, other things being equal, a great deal of careful study is given to the maintenance of as high a current efficiency as is economically possible.

Current leakage in a well-designed plant should be small. It will vary with the voltage on each circuit and the care taken to keep the tank surfaces in a good, clean condition. The higher the voltage on any circuit, the greater will probably be the leakage. The amount of leakage may approximately be determined by opening the circuit in the middle and taking the ammeter reading when the voltage is normal. As this method applies the full voltage to but half the tanks, however, the indicated leakage is apt to be somewhat higher than the actual amount. Another method is to compare ammeter readings at several points in the circuit, care being taken to guard against the stray fields that exist in the neighborhood of conductors carrying heavy currents. Leakage through the woodwork of the tanks should be negligible, provided they are kept in proper condition, and it may be assumed that the largest part of the leakage is through the circulating system, by the current being shunted around the middle tanks in the circuit, as the circulating system is in parallel with the depositing system. To prevent this leakage as much as possible the resistance should be made as high as possible by having the overflow pipes of considerable length and small cross section. Where the leak occurs to the ground, there is usually evidence on account of the copper deposited at the point where the current leaves the electrolyte.

overflow pipe

The greatest part of the loss in current efficiency is due to short circuits in the tanks. These are caused by the following conditions: the new starting sheet may curl after a few hours in the tank, and unless this is discovered and rectified a bad short circuit may result. To prevent this occurrence the starting sheets are generally removed from the tank, straightened, and replaced after a certain number of hours working. If the electrodes in the tanks are not properly aligned, there will result more or less short circuits owing to the unequal current distribution in the tank. The tank men when working on top of a tank may kick an electrode out of place and neglect to replace it properly. As the anode dissolves away, pieces of the scrap may fall off and rest against the cathode.

Except at a low current density it is not possible to produce a perfectly smooth deposit with a cathode of any considerable age, and under normal working conditions the cathodes soon become more or less rough. When this occurs the resistance between the anode and the projecting part of the cathode becomes less, and there is consequently a greater tendency for the current to flow across this part, increasing the current density at such a point and aggravating the condition. If not corrected in time, the roughness will develop into trees which bridge across the space between the anode and cathode, resulting in a dead short circuit which may stop all depositing in that particular tank. To prevent such a condition, the tank men continually patrol the tanks with voltmeters and long copper rods. When the voltmeter indicates the presence of a short circuit, the rod is swept across the space between the anode and the cathode and the projection broken off.

Deposition of hydrogen at the cathode is due to an insufficient amount of copper ions to carry the current. This condition may be caused by too low a circulation rate or by the circulation being unevenly distributed between the electrodes. It may also be caused by the copper content of the electrolyte being too low or the acid content being too high. The usual cause is probably an inefficient distribution of the circulation throughout the tank. The current efficiency may be reduced as much as 5 to 10 per cent, due to this cause.

Electrolyte Purification.—As the impurities in the anode accumulate in the electrolyte, the resistance of the latter increases, resulting in a greater power consumption, and there is also danger of the cathode being contaminated. This contamination is in addition to the contamination from adhering slime and is due to the fact that the deposited metal on the cathode is always more or less porous. This porosity permits a certain amount of the electrolyte to become entrained, and contamination from this source will not be removed by the usual washing received by the cathode prior to its charging into the wire-bar furnace. The higher the current density, the greater the tendency for porous cathodes. The addition of a small amount of glue to the electrolyte results in giving a denser deposit, but usually increases the resistance of the solution. *Blue stone* The remedy for such contamination is to keep the electrolyte as pure as possible by constant withdrawals and replacement with fresh solution. The purification of tankroom solutions is a source of considerable expense unless the impurities have a marketable value.

The various methods of purifying the electrolyte are by the manufacture of bluestone and by the use of insoluble anode tanks with or without the recovery of the sulphuric acid.

In the manufacture of bluestone, the hot electrolyte is passed through towers containing shot copper until the free acid is brought down to about 1 per cent. The solution is then concentrated with steam coils in lead-lined tanks and sent to the crystallizing tanks where the copper sulphate is allowed to crystallize on lead strips. These crystals may be sold or else redissolved and sent back to the tankroom. The mother liquor from this crystallization contains the impurities, and if the impurity is of value, such as nickel sulphate, it may be further evaporated and the nickel sulphate crystallized out, after any traces of copper have first been removed. Otherwise the foul solution is wasted after precipitating out the remaining copper on scrap iron.

When using insoluble anodes, the solution to be purified is passed through a series of tanks containing anodes of hard lead. These tanks may be used either for the reduction of the amount of copper in the electrolyte or for the complete removal of the copper prior to the final treatment of the solution. Where it is simply desired to reduce the amount of copper in the electrolyte, the latter is circulated through the tanks at a high rate and returned to the tankroom. The high rate of circulation is desired in order that the efficiency of deposition may be as high as possible and also that the quality of the cathode produced be high enough to be sent to the wire-bar furnace. Where it is desired to remove the copper completely, the circulation is reduced. There are usually three to five tanks in series, and the copper from the first tank is generally of good enough quality to send to the wire-bar furnace. The product of the remaining tanks will, to a large extent, depend upon the composition of the electrolyte being purified. As the copper becomes depleted, arsenic and antimony are deposited as a sludge, which is generally sent to the blast furnace, if there is one at the plant, or else treated by special methods. The last tank eliminates the last traces of copper from the electrolyte. The efficiency of these tanks is very low, the average for the series being about 20 per cent or less.

If arsenic and antimony are the impurities to be eliminated, the solution is returned to the tankroom. If there is a large amount of soluble sulphates, such as iron, nickel, or zinc, the solution from the insoluble anode tanks is either sent to the sewer and the acid content wasted, or else it may be concentrated by heating to such a point that, upon cooling, the objectionable sulphates are crystallized out. The mother liquor, which is high in free acid, is then returned to the tankroom.

The use of the insoluble anode requires considerable power, but the investment required is small, whereas a large investment is required for the manufacture of bluestone. If, however, large amounts of solution are required to be purified, there is danger of depleting the electrolyte of copper to too great an extent. This is partic-

ularly true when the anode contains considerable amounts of nickel or iron, so that there is much less copper being dissolved than deposited. In such a case it becomes necessary to add copper to the electrolyte by means of bluestone or by trickling hot electrolyte through towers containing shot copper. On the other hand, with a pure anode there is a building up of the copper contents of the electrolyte, and this excess will have to be removed by one of the above methods.

The insoluble tanks are usually in two groups, the first of which has a high rate of circulation and removes the bulk of the copper, the second group removing the balance of the copper together with such arsenic and antimony as may be present. As the power consumption of insoluble anode tanks is high, an attempt has been made to eliminate the first set by utilizing the principle of the stratification of the electrolyte.¹ In this method advantage is taken of the fact that at the face of the anode there is a downward flow of the electrolyte due to the increase of copper concentration, while at the face of the cathode there is an upward flow due to the decreased copper concentration. By withdrawing the main bulk of the electrolyte from the lower part of the tank and about 10 per cent from the upper part, there is obtained from the lower outlet a solution high in copper and relatively low in acid, while from the upper outlet the solution is low in copper and relatively high in acid, the copper being less than is usually obtained from the outlet of the first group of insoluble anode tanks. As the impurities do not segregate, the solution from the upper outlet contains practically the same amount of impurities as the average solution in the tanks. This method thus saves the extra cost of one group of insoluble tanks and produces a cathode similar to those obtained from the regular refining tanks, with the expenditure of little, if any, more power than required for the production of regular cathodes.

The cathodes from the electrolytic refining, having been washed, are sent to the wire-bar furnace. This type of furnace is similar to that described under anode casting (pp. 249-251), but the operation requires more care, particularly in the poling operation and casting. Great care must be taken to have the metal at the proper heat, as cold copper will result in bars that are porous. Hot copper will absorb gases from the gases of combustion, and these gases will be liberated on cooling, giving porous copper.

Overpoling causes the surface of the bar to rise and throw out a worm, and the resulting metal will very likely be brittle. The causes of overpoling are not definitely known, but it is believed that sulphur plays an important part.

Refined copper is cast on the Walker wheel or the straight-line machine, as described previously. The Clark wheel is a modification of the Walker wheel with the molds placed radially instead of tangentially, and bars of any length can readily be cast thereon.

The commercial forms of cast copper are wire bars, cakes, slabs, ingots, and ingot bars. Wire bars are bars of approximately square cross section, the length varying from 40 to 60 in., the width and depth from 2½ to 4 in. The ends are usually tapered to facilitate admission to the rolls in the rolling mill. The weight of wire bars varies from 135 to 300 lb. according to the demands of the consumer. Cakes are square, or rectangular castings, varying in dimensions from 14 × 17 in. to 42 × 42 in. The thickness depends upon the weight desired for any particular cross section and varies from 2 to 8 in. Cakes under 28 × 28 in. are generally cast on the casting machine, the larger ones being cast in open iron split molds, placed on a copper base. Slabs are long, thin, shallow bars, usually with square ends. Ingots are small castings weighing about 20 to 25 lb. and have one or two heels cast to permit being broken up easily by the consumer. Ingot bars are bars consisting of several ingots end to end.

Cakes and wire bars are also cast vertically to reduce the amount of "set" surface.

¹ PYNÉ, *Trans. Am. Electrochem. Soc.*, Vol. 28, p. 111.

When casting refined shapes the molds are painted with bone ash. This gives a smoother surface than the pulverized silica used in the anode casting. For satisfactory work, the bone ash must be thoroughly calcined, be free from grease and organic matter, and must be very finely ground, 95 per cent to pass 200 mesh. It must be applied uniformly to the molds, or the excess will cause the bars to be pitted.

When casting refined copper, great care must be used. If the mold is filled too rapidly, there will be a tendency for some of the copper to run up the side of the mold and set there. Excessive vibration of the casting machine has the same effect. Unless these fins are removed by chiseling before rolling, they will be rolled into the finished rod and cause trouble. Particles of ladle lining, charcoal, etc., are known as "fish" and are removed during the casting and before the metal has set by the use of a long-handled, flat-bladed tool.

Over- and undersized bars are caused by the molds being out of level, warped, or by the carelessness of the operator in filling the molds. An oversize bar may cause trouble in the rolling mill by crowding the roll and thus producing a fin which is rolled into the product. Undersized bars cause no damage in the mill, but add to the expense of rolling owing to the shortage in weight, which requires more pieces to be rolled for the same tonnage.

As the bars set, they are sprayed with water and dumped into a water-filled bosh to cool sufficiently to permit of handling and inspecting. The inspection is very rigid, and bad-looking bars are rejected and remelted. The bars that pass the inspection are stamped with the furnace and charge number for future reference in case of complaint.

The quality of the copper is determined by assay and by taking a sample for conductivity. While the assay will show the purity of the metal, which generally is about 99.93 to 99.96 per cent, the conductivity test is relied upon to show the physical qualities. Small amounts of impurities have, in general, a very marked effect upon the conductivity of copper, and while those elements which make copper brittle do not, for the most part, affect the conductivity to any great extent, their presence will be detected in drawing the wire for conductivity purposes.

Treatment of the Anode Slime.—The anode slime contains all the silver and gold that is present in the anode, disregarding the insignificant amount lost in the cathode. It will also contain varying amounts of arsenic, antimony, selenium, tellurium, nickel, and a certain amount of copper, depending upon the degree of refining the anode.

At the tankroom the slime is generally passed over a coarse screen to remove large pieces of copper, such as anode scrap and cathode nodules, and is pumped over to the silver refinery, where it is allowed to settle in tanks of large cross section. The supernatant liquor is decanted and returned to the tankroom. The first step in the treatment is the removal of the copper content, which may vary from 15 to 50 per cent. There are several methods of accomplishing this. The earlier method was to agitate the slime with a mixture of sulphuric acid and niter in a lead-lined vat by means of mechanically rotated paddles, heat being applied by means of steam coils in the bottom of the vat. The niter oxidized the copper, which was converted into copper sulphate. When the reaction was complete, the residue was washed and allowed to settle, and the liquor decanted and sent to the tankroom. The mud was then filter-pressed and sent to the refining furnaces. A modification of this process was in agitating the mixture by means of compressed air instead of the paddles.

The serious objection to the use of this method, aside from the expense of the niter used, was in the formation of large amounts of sodium sulphate, which went back to the tankroom with the copper sulphate, and increased the resistance and specific gravity of the electrolyte. In order to avoid this and to do away with the expense

of niter, the slimes are given an air roasting with sulphuric acid present, after which they are boiled with acid to remove the copper sulphate. This method has entirely supplanted the former one.

The slime is either spread in thin layers in trays or in a thin layer on the hearth of a roasting furnace, and heated with a large excess of air to a point where oxidation occurs, but below the point where the slimes start to sinter. The slime may or may not be rabbled during the roasting, depending upon the existing facilities for catching the flue dust that is formed. When no rabbling is done, the time for the oxidation is necessarily of longer duration; a sulphuric-acid spraying may also be given. When the roast is completed, the slime is removed from the roasting furnace and conveyed in cans to the boiling tank, where it is boiled with dilute sulphuric acid, which removes the oxidized copper as copper sulphate. It frequently occurs that in this boiling a considerable amount of silver goes into solution, and this must be precipitated by the addition of the necessary amount of raw slime, the metallic copper of which reacts with the silver. The objection to this procedure is that an excess of the raw slime is generally added so that the finished slime contains more copper than is desired.

By any of the above methods the copper in the treated slime may be reduced to about 1 per cent, and the slime is then ready for the furnace treatment. The furnaces used are generally small basic-lined reverberatories, or else small basic-lined tilting furnaces, the latter being preferable on account of the smaller amount of precious metal tied up in the furnace linings, an item of no small importance. The furnaces may be fired by fuel oil, gas, or powdered coal.

The slime is charged into the furnace with a small amount of soda in order to thin out the slag formed on the melting down. The slime readily melts, and during the melting a very fusible thin slag is formed, which is drawn off as it is formed, so as to keep the surface of the slime from being blanketed and slowing down the melting. When the charge is completely molten, further additions of soda are made and the charge is oxidized by compressed air through iron pipes inserted under the surface of the charge. During this oxidation, the great bulk of the impurities are removed and the charge gradually assumes a metallic aspect. When the soda slag will remove no further impurities, the metal is covered with niter and the oxidation continued. This procedure brings the bath up to a good grade of doré, 980 to 990 silver plus gold, and the metal is then ready for casting into doré anodes. The niter slags formed during the last operation are generally charged back into the furnace with the succeeding slimes, the soda slags being sent to the blast furnace for recovery of the silver and copper content, or treated for the recovery of tellurium before resmelting. In some plants the soda slags are returned to the anode furnaces, but this practice is not to be recommended, as the various impurities in the slag enter the anode to a considerable extent, thus making them circulate in the system and usually giving trouble with the solution of the anodes in the tanks.

The doré, which is the name given to the high-grade mixture of silver and gold, is then cast into anodes by the use of a hand ladle. The anodes vary in size at the various plants, depending upon the process for removing the silver. For the average electrolytic process the size will be approximately $12 \times 6 \times \frac{1}{2}$ in. The anodes are then sent to the parting plant, where the silver and gold are separated. For this purpose there are two well-established processes in use at the present time, the sulphuric acid and the electrolytic, described in Chap. X.

Should there be platinum or palladium present in the doré, these metals will accompany the gold. The methods of extraction are chemical or electrolytic. In the former the gold mud is boiled with strong sulphuric acid and a small amount of nitric acid or niter, which dissolves practically all these metals. The resulting solution is then passed over copper to precipitate the silver and the platinum and palladium. The

Tilt
Furnace
Treatment

Anode
Slag

Anode
Pt. - Pd
Recovery

resulting sludge is then dissolved in aqua regia, which dissolves the platinum and palladium but leaves the silver as silver chloride. From this solution the platinum and the palladium are recovered by the use of ammonium chloride and ignited to give a metallic sponge of a purity of 98 per cent or better.

Metal Losses in Refining.—The question of metal losses in the refining of copper, with its accompanying silver and gold, is one of great importance. The sources of losses are numerous, and vigilant attention is required to keep them within proper limits. The usual sources of losses taken in the order the material passes through the plant are as follows: weighing, sampling, assaying, anode slag, anode flue dust, cathode loss, wire-bar slag, wire-bar stack, weighing, slimes loss in silver process, gold in fine silver, silver in fine gold. There are also certain other losses, such as those from solution and theft.

In weighing, considerable loss may be experienced through lack of proper care of the scales and careless handling of test weights. In the average plant these points are generally given careful attention. A usual source of error in weighing lies in the taring of the cars carrying the incoming blister. These should be carefully tared at stated intervals and particularly after any repair work has been done on the car, no matter how slight. An error of considerable magnitude may be caused in weighing cars that are not properly protected from the wind while on the scale.

Sampling errors may easily run into large figures, and every possible precaution should be taken to see that the best practice is in use. This is particularly important where the blister copper contains considerable silver and gold. The question of moisture in blister copper is important. The average copper is very porous and will absorb up to 0.5 per cent of moisture while apparently quite dry on the surface. A frequent source of error against the refinery lies in the occluded moisture from quenching the copper as it comes from the molds at the converters. This may amount to as much as 0.25 per cent and can be determined only by carefully drying the copper at a temperature sufficient to drive off the moisture, but not sufficient to oxidize the copper.

In assaying, errors frequently occur through the laboratory using methods that give consistently low results or consistently high results. Unless the splitting limits are quite close, so that such methods are brought to the front by the frequency of umpire assays, a serious error may be introduced.

Anode and wire-bar stack losses will, to a large extent, depend upon the nature of the material being treated in the furnace. The apparent magnitude is not large judging from baghouse tests, particularly where, as is almost always the case, waste-heat boilers are installed.

Anode and wire-bar slag losses may, and frequently do, amount to a considerable item. These slags will run in the neighborhood of 40 to 50 per cent copper and must be re-treated in a blast furnace for the recovery of the copper. It is necessary to slag off the silica content, and, as the slag from the blast furnace will contain some copper, it is apparent that the more slag made in the reverberatory furnaces the more slag will be made in the blast furnace with its accompanying copper loss. This loss is particularly serious in cases where the refinery slags are treated in a black-copper furnace, as in such a case the resulting slags are very much higher in copper with a correspondingly greater copper loss to the refinery.

Cathode losses constitute one of the largest items of silver and gold losses in the process. There is always a certain amount of anode slime floating in the electrolyte and, if the cathode is rough, a large amount of this may be caught and thus pass into the wire bars, where it is lost. This loss may be controlled by careful supervision over the factors affecting the cathode deposit, such as proper refining of the anode, current density, and rate of circulation.

Loss
by furnace
gases

In the treatment of the anode slime in the silver building there is opportunity for great losses in the furnace gases. In former years these losses were of considerable magnitude, and it is only with the recent installations of the Cottrell system that their real magnitude has been appreciated. At the present time with properly designed Cottrell apparatus the losses from the silver-refinery roaster and furnace gases have been reduced to a very low point, though, even with this safeguard, careful watch must be kept on every step in the process for unsuspected leaks that, in the course of a year, may be considerable.

In the production of fine silver there is always loss of gold due to the difficulty of keeping the gold mud completely out of the silver crystals. Similarly, the refined gold always contains some silver. The partial cure for such losses is in proper care of the doré anode bags so that the loss is reduced to a minimum.

The amounts of the losses in cathodes, silver, and gold are kept continually before the management through the daily assays, so that any tendency to go wild should be promptly discovered and means taken for correction.

Losses by theft may amount to a large item, particularly if there is much small stuff such as copper scrap or scrap wire received. Such copper is easily carried out of the plant in dinner pails, clothing, etc., and a careful watch must be kept to keep this at a minimum. A thorough policy of prosecution when an employee is caught will go a great way to prevent similar occurrences in the future.

In general, it may be stated that in a well-conducted refinery the copper losses will average about 7 to 8 lb. per ton of cathodes produced. Silver and gold should break about even, provided the assays are uncorrected; if corrected, the silver loss will be about 2 per cent and the gold loss about 1 per cent of the contents of the anode, as these figures are the average corrections for the usual type of copper received by the refineries.

Properties of Refined Copper.—The melting point of pure copper is 1083°C., which may be slightly reduced by the presence of small amounts of cuprous oxide. The boiling point is in the neighborhood of 2310°C., but experimental difficulties have prevented a precise determination.

The latent heat of fusion is 43.3 cal. per g., and its specific heat varies with the temperature. The National Bureau of Standards gives the latest determination as

$$C = 0.0917 \times 0.000048(t - 25)$$

where *t* is the absolute temperature.

The electrical conductivity of copper varies greatly, depending upon the presence of minute quantities of various impurities. The following tables compiled from various sources, together with experimental work by the writer, show in a general way what may be expected. It must be kept in mind, however, that the presence or absence of oxygen in the copper may greatly vary the results. When the impurity is in solid solution, its effect is generally much greater than if it is in some other form. In these tables the conductivity of pure copper is arbitrarily taken at 100 per cent.

PER CENT	CONDUCTIVITY, PER CENT	PER CENT	CONDUCTIVITY, PER CENT
Aluminum:		0.050.....	95.0
0.000.....	100.0	0.100.....	88.0
0.006.....	99.0	0.250.....	75.0
0.050.....	84.0	Arsenic:	
0.100.....	67.0	0.000.....	100.0
Antimony:		0.005.....	98.5
0.000.....	100.0	0.010.....	95.5
0.020.....	97.5	0.050.....	85.0

PER CENT	CONDUCTIVITY, PER CENT	PER CENT	CONDUCTIVITY, PER CENT
0.100.....	75.0	0.070.....	60.0
0.200.....	60.5	0.150.....	42.0
0.500.....	40.0	Silver:	
Bismuth:		0.000.....	100.0
0.000.....	100.0	0.100.....	99.8
0.005.....	100.2	0.500.....	97.5
0.010.....	99.5	1.000.....	95.5
0.050.....	98.5	Sulphur:	
Cadmium:		0.000.....	100.0
0.000.....	100.0	0.050.....	99.5
0.025.....	99.9	0.100.....	98.0
0.050.....	99.6	0.250.....	97.0
0.100.....	99.0	Tellurium:	
0.250.....	97.0	0.000.....	100.0
0.500.....	96.0	0.010.....	100.0
Lead:		0.025.....	99.0
0.000.....	100.0	0.050.....	99.0
0.050.....	99.5	0.100.....	98.5
0.100.....	99.0	Tin:	
0.300.....	98.5	0.000.....	100.0
Nickel:		0.050.....	98.0
0.000.....	100.0	0.100.....	93.0
0.005.....	99.0	0.500.....	75.0
0.010.....	98.5	Selenium:	
0.100.....	93.0	0.000.....	100.0
0.400.....	75.0	0.010.....	99.0
1.000.....	55.0	0.050.....	98.5
Phosphorus:		0.100.....	98.0
0.000.....	100.0	Zinc:	
0.005.....	100.5	0.000.....	100.0
0.020.....	96.0	0.050.....	98.5
		0.100.....	96.5

The effects of the various impurities on the mechanical properties of copper may be summarized as follows:

Arsenic toughens, hardens, and increases the tensile strength of copper when present up to at least 1.5 per cent. It will not impair the forging properties when added in amounts up to 0.5 per cent and invariably improves the forging properties of impure copper.

Antimony hardens and strengthens copper, though not to the same extent as arsenic. It is not detrimental in amounts up to 0.5 per cent if other impurities are absent and the proper amount of oxygen is present.

Bismuth has by far the most deleterious effect on copper of any impurity; 0.02 per cent makes copper red-short, 0.05 per cent makes it cold-short, and 0.1 per cent makes it very brittle. The injurious effects of bismuth may, to a certain extent, be counteracted by the presence of oxygen.

Cobalt is said to confer greater durability at high temperatures and toughens, hardens, and strengthens copper in the cold.

Iron, when present in amounts in excess of 1 per cent, makes copper hard and brittle.

Lead when present alone in copper reduces the strength, ductility, and toughness of copper, as the latter has no solvent power for lead. The latter, therefore, honey-combs the structure more or less uniformly and greatly weakens it above ordinary temperatures. In the presence of oxygen and arsenic, lead may occur to some extent without ill effects. In the absence of oxygen and arsenic, 0.1 per cent lead will make copper unworkable, but with oxygen and arsenic present this amount is claimed to make copper roll better.

Nickel in small amounts—a few tenths of 1 per cent—imparts strength, toughness, and increased resistance to deformation at high temperatures. In Germany, copper containing a small amount of nickel is preferred to arsenical copper for the manufacture of firebox sheets.

Oxygen in commercial impure wrought copper is essential where the metal has to withstand repetition of small stresses, exposure to atmosphere, influence of corrosive agents, etc. Its presence offsets the harmful effects of bismuth, lead, etc. Copper containing too much oxygen is cold-short, and, if the oxygen is in great excess, the metal is also hot-short.

Silicon, when added to copper in amounts up to 3.5 per cent, increases the hardness and assists in the production of sound castings. With 6 per cent silicon, copper is brittle. A small amount of silicon, 0.1 per cent, added to copper will increase the fluidity of molten copper so that castings free from blowholes can readily be produced.

Silver in copper benefits its mechanical properties and has no effect upon its hot-working properties.

Sulphur in copper forms a highly dangerous brittle constituent and is very detrimental to the mechanical working of copper. When present, its bad effects may, to a large degree, be counteracted by the addition of manganese or aluminum.

Oxygen-free copper (OFHC) having qualities superior to regular fire-refined copper is produced by a patented process developed by the United States Metals Refining Co. In this process the last traces of oxygen are removed in the refining process, and the metal is cast in a reducing atmosphere.

Another type of oxygen-free copper is produced by first depositing a brittle copper cathode, which is broken into pieces of the desired size. These pieces are briquetted by compressing at a pressure of 20,000 lb. per sq. in. The briquettes are then sintered in a reducing atmosphere and pass to an extrusion press, from which solid metallic copper is produced in the shapes desired.

Electric melting of copper cathodes has been developed by the International Nickel Co. This company has installed electric arc furnaces which are continuously charged with cathodes and which produce finished shapes without the usual blowing and poling operations of the refining furnaces.

James B. Scott
45

CHAPTER X

REFINING OF GOLD AND SILVER BULLION

BY ELY J. WAGOR¹

Parting.—Gold and silver are so intimately associated in all classes of bullion produced in either mining or metallurgical operations that refining processes must not only consider the elimination of the base metals present in the alloy, but also the “parting,” or separation, of the gold and silver. This separation is effected by dry, wet, or electrolytic methods.

The dry method is based on the conversion of the silver in the alloy to a chloride or a sulphide while the bullion is in a state of fusion. This principle finds application in the so-called Miller process, in which chlorine gas is passed through the molten metal, converting the silver and base metals into chlorides which pass off as fumes or are skimmed from the surface of the molten charge. The use of this method is, of course, restricted to bullion carrying limited amounts of silver.

The wet method depends upon the solubility of silver and the insolubility of gold either in nitric acid or in boiling concentrated sulphuric acid. In practice, the sulphuric acid-parting process has gradually superseded the older and more expensive nitric-parting process.

The electrolytic method is essentially a wet method, but is based on electrochemical rather than simple chemical reactions. Electrical energy is used to produce chemical changes by the passage of a current through an electrolyte. The Moebius, Balbach, and other silver-refining processes for refining bullion in which silver predominates in the alloy depend on the solubility of silver and the insolubility of gold at one electrode and a deposition of silver at the other under current action in a nitric electrolyte. The only differences in these silver-refining methods are certain mechanical variations and arrangements in the equipment used. The application of electrolytic parting to bullion in which gold is the predominant metal is found in the Wohlwill process of gold refining based on the solubility of gold and the insolubility of silver at one electrode and the deposition of gold at the other, under current action in a chloride electrolyte. MNO₃

In this general outline of methods used in the parting of gold-silver alloys, detailed consideration will first be given to the Miller process, or the refining of gold bullion by the use of chlorine gas.

Miller Process of Chlorination.—The equipment and the operation of the Miller process installation in the Royal Mint at Ottawa, Canada, are described by Messrs. Cleave and Bond.²

This plant operates 16 chlorination, 2 tilting, and 4 ordinary furnaces. The chlorination furnaces are of fire clay, cylindrical in shape, with an inside diameter of 9 in. and a depth of 18 in. This battery of furnaces is connected with a large flue chamber provided with a spraying system for washing and cooling the fumes developed in the operation of chlorination. Provision is made for the recovery of values in the water through which the fumes have passed in a series of filters and settling tanks. Chlorine gas is supplied from cylinders housed in a brick leakproof closet. The gas is

¹ Superintendent, Melting and Refining Department, U. S. Mint, Denver, Colo.

² *Eng. Mining Jour.-Press*, Feb. 3, 1923.

conducted through a heavy lead pipe extending along the top of the flue chamber with a branch leading to each furnace fitted with a valve for regulating the flow of gas to the different units.

Clay crucibles are used having a height of 11¼ in. and a diameter at the top of 5¾ in., tapering to 3¼ in. at the bottom. These are provided with slotted covers to allow inserting and withdrawing the clay pipe stems, which are about 2 ft. in length and ¾ in. in diameter. In the operation of chlorination, the clay crucibles are placed inside graphite crucibles as a safeguard against leakage or breakage.

Bullion for treatment is first melted in a tilting furnace in charges of 7000 to 8000 oz. After the chlorination equipment is brought to a red heat, 600 to 700 oz. of the molten bullion from the tilter is poured into each crucible, sufficient borax having been previously added to form a cover ¼ in. in thickness. The pipe stems are forced to the bottom of the crucibles and held in position by clamps. The gas is turned on slowly at first, and the flow is gradually increased to the maximum where no free chlorine is given off. The base metals are immediately attacked, and pass off in dense fumes, which are drawn into the chamber through the furnace flues.

After the base metals have been practically eliminated, chloride of silver is formed, which floats on the surface of the gold beneath the borax cover. When chlorination has been completed, determined by a brownish stain formed on a clay rod held in the fumes, the remaining silver chloride and other impurities are baled off. The gold is then cleaned up with bone ash and poured into a mold, and the crucible is ready for another charge.

The time necessary for the completion of the operation depends, of course, on the amount of silver and base present in the bullion. Bullion containing 800 parts gold, 150 parts silver, and 50 parts base metal per 1000 requires 1¾ hr. for chlorination, and during this period it is necessary to skim off the silver chloride formed three times to prevent it from overflowing the crucible.

The chlorides skimmed off during the operation are remelted in a No. 45 graphite crucible, and sodium carbonate is slowly charged in on the top of the melt. This effects a partial reduction of the chloride to metallic silver, which, in settling to the bottom of the crucible, carries with it the gold contained in the chloride. The charge is allowed to cool sufficiently to solidify the metal, and the still molten chloride is poured into shallow molds. The silver containing the gold is cast into anodes and refined by the electrolytic Moebius process.

The chloride cakes are treated in a tank with boiling water to remove the base chlorides, and then placed in another tank in alternate layers with iron plates for reduction of the chloride to metallic silver. This silver will sometimes approximate a fineness of 999. The gold from this process will average 996.5. With a plant as outlined, it is possible to produce 250,000 oz. of refined gold in a 48-hr. week.

Sulphuric Acid Parting.—This process has been described in detail by Schnabel in his "Handbook of Metallurgy," by T. K. Rose in "The Metallurgy of Gold," and by others, and consists essentially in four operations as follows: (1) blending of the bullion to required fineness and preparation for parting operation; (2) dissolving of the silver by sulphuric acid; (3) treatment of the residues for gold; (4) recovery of the silver from sulphate solution.

Blending of the Bullion.—The bullion must be blended or mixed in such proportion that a melt of prescribed weight must contain certain definite proportions of gold, silver, and base metals. The make-up varies in different plants, ranging from 2½ to 4 parts of silver to 1 part of gold according to the amount of copper present. The sulphates of the base metals present in the bullion are only slightly soluble in concentrated sulphuric acid, and care must be exercised in keeping the base-metal content within certain limits. The copper present should never exceed 10 per cent, and, if

Borax
cover

Bone
ash +
Hiter

Skimmed
of all residues
with solution
cont.

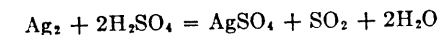
possible, should be kept under 6 per cent. Lead, up to 5 per cent, does not materially interfere with the process. The bullion is melted in graphite crucibles in melts of 3600 to 6000 troy oz.

In order to expose the maximum amount of surface to the action of the acid, these melts are either granulated or poured into thin slabs. Granulations are made by pouring the molten metal, in a small stream with a whirling motion, into large copper tanks filled with cold water. After pouring, the water is drawn off and the granulations are dried on heated trays of either copper or iron. Slabs for parting are cast into shallow iron molds ¾ in. deep by 9 in. wide by 15 in. long. The advantage claimed for the slabs over granulations is in the less violent action of the acid, thus affording better control of the dissolving action.

Solution of the Silver.—This is effected in cast-iron pots of fine-grained, compact white iron containing a small percentage of phosphorus or silicon. These pots are usually hemispherical in shape, 40 in. or less in diameter, with a 1½- to 2-in. wall. Covers, either of cast iron or heavy sheet lead reinforced with iron, are fitted to the pots with lead-pipe connection for carrying off the fumes of sulphur dioxide and openings for charging with metal and acid. Dissolving kettles have capacities ranging from 3600 to 16,000 troy oz.

For each part of silver in the bullion, 2 to 2½ parts by weight of commercial concentrated sulphuric acid, 66°Bé., is added. Heat to facilitate action of the acid is usually applied by wood fire, and extreme care must be used in regulation of the temperature in controlling the ebullition. One-half of the total acid required is added at the start, and the remainder from time to time as the action warrants. During action, the charge must be stirred occasionally with an iron tool. The time required for complete solution of the silver varies from 6 to 12 hr., depending on the amount of base metal present and the care with which repeated stirrings are made. The acid vapors are led to a condensing chamber where particles of silver sulphate carried over may be deposited. SO₂ may be recovered in leaden chambers as sulphuric acid, ferrous sulphate, or hyposulphite.

The reaction represented in the process would be



The base sulphates are only slightly soluble and, therefore, have a tendency to stay with the gold residues; their chemical reactions are, as a rule, quite complex. In the end, a small amount of cold acid is added to help clear the solution. The clear solution of silver is ladled or siphoned into lead-lined tanks partly filled with hot water, in which the precipitation of the silver is effected.

Treatment of the Residues for Gold.—Repeated boilings of the gold residues with fresh concentrated acid are necessary to remove the remaining silver and base metal. Often as many as seven boilings are necessary. Residues are finally washed with hot water or hot dilute acid to remove the anhydrous sulphates. The gold is pressed, dried, and melted with a flux of niter and bone ash, and is cast into bars having an average fineness of 995.

Recovery of Silver from Sulphate Solution.—Silver may be recovered from solution by precipitation with copper, iron, or ferrous sulphate. The most common method is by copper replacement, in which the solution is brought to a concentration of 24°Bé. by steam, and silver is precipitated as cement silver on scrap copper placed around the sides and on the bottom of the tank, or, better, on slabs of copper hung vertically in the solution. After the silver is completely precipitated, it is allowed to settle and the clear solution siphoned off. The silver is removed to a wooden filter tank where it is thoroughly washed. After pressing into cakes, it is dried and melted,

Flux
with
Niter
&
Bone
ash.

giving a product, after fluxing, 990 to 998 fine. Further refinement, if necessary, may be accomplished by cupellation.

In the iron method of recovery, the silver sulphate is separated out in solid form and packed in layers alternating with layers of sheet iron. This method is attended with much heat and considerable gassing, but is more economical. The silver may also

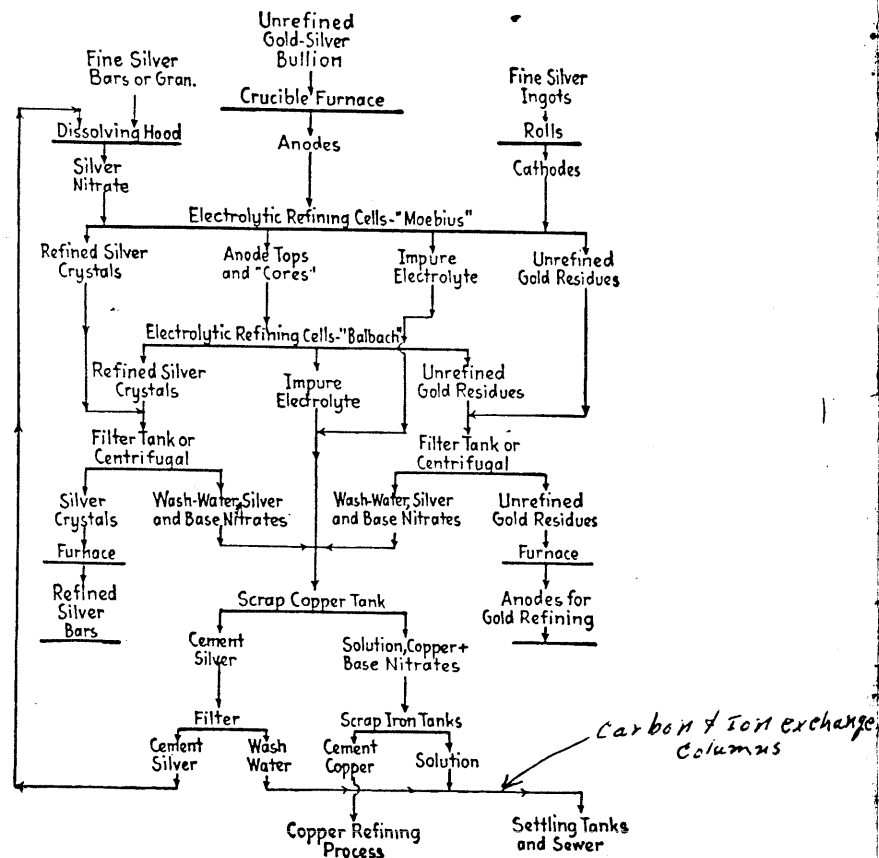
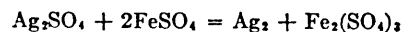


DIAGRAM 1.—Silver refinery flow sheet.

be recovered by running a hot solution of ferrous sulphate through a filter containing crystals of sulphate of silver according to the reaction



The ferric sulphate may be reduced by iron and used again for reduction of the silver.

Where copper is used for precipitating the silver, the copper in the mother liquor may be crystallized as copper sulphate by alternate evaporation and crystallization on lead sheets suspended in lead-lined tanks.

Electrolytic Processes.—Electrolytic methods of refining have, to a large extent, replaced or supplemented the acid-parting process not only in large-scale operations but also in the smaller plants, in private as well as government-operated refineries. The advantages over acid parting may be summed up as follows: (1) lower cost of

operation, (2) higher standard of refined product, (3) neatness of operation and absence of noxious fumes, (4) recovery of the platinum metals as by-products.

The Moebius and Balbach systems of silver refining find application in the treatment of bullion ranging from a few points of gold (doré silver) up to 350 parts per 1000; the Wohlwill process of gold refining, in the treatment of bullion containing 850 or better of gold per 1000.

The Moebius Process.¹—Wooden tanks of pitch pine may be used, thoroughly tarred to prevent leakage. These tanks, 2 ft. wide by 12 ft. long, are divided by transverse wooden partitions into seven compartments or units. In each compart-

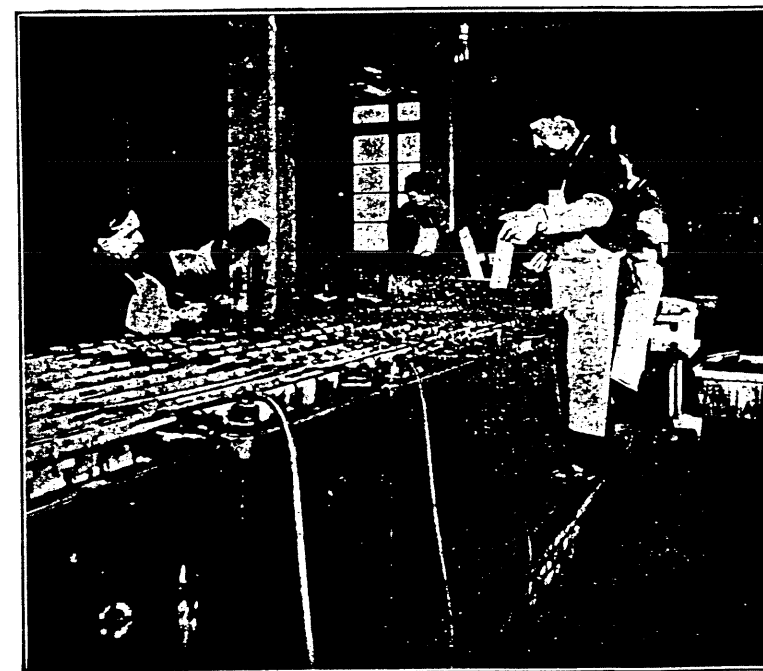


FIG 1.—Moebius cells. Anode shown at left. Stripping cathode at right.

ment are suspended three rows of anodes and four rows of cathodes. The anodes are suspended in muslin bags or cloth frames which serve to collect the undissolved metals and prevent contamination of the deposited silver. The cathodes are thin rolled strips of pure silver, which are straddled by mechanically operated wooden scrapers removing silver crystals as fast as they are deposited, and serving to keep the electrolyte uniform by gentle agitation. A removable tray is placed under the electrodes for removal of the silver, and all arrangements, electrodes, scrapers, etc., in each unit are carried on a frame and can be lifted together from the refining tank.

The electrolyte is a weak solution of silver nitrate containing free nitric acid, though the operations may be started with a dilute solution of nitric acid.

In the treatment of doré silver bullion the permissible current density varies from 20 to 28 amp. per sq. ft. of cathode surface, and the potential across the electrodes, or of the unit, is 1.4 to 1.5 volts. At this density about 40 per cent of the daily output

¹ For a description of this process as practiced at Maurer, N. J., see Griswold, *Eng. Mining Jour.*, Vol. 107, p. 789, May 3, 1919.

of each unit is permanently held in stock in cathodes and electrolyte. The energy consumption is 13.2 watt-hr. per oz. of silver deposited.

The anode mud, consisting of gold, some silver, lead as peroxide, and other insoluble metals, is removed periodically from the bags and, after washing, is parted by acid or other means.

The silver is deposited in a loose crystalline form easily removed from the cathode, although at lower current densities it is deposited in a more adherent form. An addition agent, as gelatin or glue in the electrolyte, to harden the deposit, is effective only when the solution is comparatively free from base metals.

Balbach Process.—The electrolyte used in this process is the same as used in the Moebius, but the anodes, instead of being suspended vertically in the electrolyte, are placed horizontally in filter frames or baskets supported on the edges of the tanks, and the silver is deposited on a cathode fitted to the bottom of the refining cell or tank. Originally, this cathode was made of silver, but the universal practice now is to use graphite plates, $\frac{1}{2}$ in. thick, cut to size to fit the bottom of the refining tank. Contact with these plates is effected by use of silver candle-shaped contact pieces cast in a special mold, and in a similar manner electrical connection is made with the anode. The anodes are cast in thin slabs and placed in the muslin-lined wooden frames or baskets with grill bottom. The insoluble residues accumulate on the underside of the slabs as the parting progresses, thus gradually increasing the resistance of the cell. The deposited silver is removed from the bottom of the cell by a long-handled scoop of wood or hard rubber, the anode basket being raised clear of the cell to facilitate the operation.

The distance between the electrodes is 4 in. and the depositing surface about 8 sq. ft. With a voltage of 3.8 per tank and a current density of 20 to 25 amp. per sq. ft., the energy consumption is 31.5 watt-hr. per oz. of silver produced, and 32 per cent (approximately) of the daily output is held in process in electrolyte and contact pieces. No agitation or circulation of the electrolyte is required in this process.

A critical comparison of the Moebius and Balbach systems is made by F. D. Easterbrook.² It is to be noted that the Balbach cell is simpler in its operation, having no moving parts. Its energy consumption, however, is greater, and its depositing surface per unit of floor area is considerably less than that of the Moebius.

An innovation in silver refining was tried for some time in the Ottawa Mint in Canada, and was described by A. H. W. Cleave.³

The cell made use of a rotating cathode and permitted a current density of 150 amp. per sq. ft. of cathode surface at a voltage of 2.5 without unduly increasing the temperature of the electrolyte. These cells were 36 in. in diameter, and the electrolyte was contained in the annular space 8 in. wide by 18 in. deep between the outer and inner walls of the cell. The cathode carrier was supported at the center of the cell and was revolved by a shaft passing through this central hollow space. The deposited silver was loosely adherent and was automatically scraped from the cathodes, falling into removable trays from which the silver was removed every 4 hr.

An interesting comparison between the Moebius and the newer type of cell was given by Cleave.⁴ In spite of the apparent advantages, it is understood the newer cell was abandoned.

The United States government in its Mint and Assay Service operates three electrolytic refineries. All classes of bullion are received for refining, except that in which

¹ Balbach Refinery, *Elec. Chem. Ind.*, Vol. 2, p. 302; THUM and EASTERBROOK, *Electro. Chem. Met. Ind.*, Vol. 6.

² *Trans. Am. Electrochem. Soc.*, Vol. 8, p. 125.

³ *Eng. Mining Jour.-Press*, Vol. 116, p. 21.

⁴ *Loc. cit.*

the base-metal content exceeds 800 parts per 1000, and electrolytic processes are used exclusively in the parting and refining operations, the Moebius and Balbach-Thum processes for silver, and the Wohlwill method for gold. Most of the refined silver is produced by the Moebius or "vertical system," the Balbach-Thum or "flat cells" being used to supplement the Moebius-cell operation in treatment of the unparted anode remnants and bullion too base to be handled by the "vertical system."

The cells used in the "vertical system" are of vitrified acidproof stoneware, either of earthenware or domestic porcelain, 44 to 48 in. long, 24 in. wide, and 18 to 24 in. deep. The electrode supports are either hard-rubber rods reinforced by a steel core, or close-grained maple sticks, rounded on one side and painted with an acidproof paint. Half-round conducting strips of either gold or silver cover the top sides of the electrode supports and are fastened to bus bars placed along the edge of the cells. The distance between electrodes varies from $2\frac{1}{2}$ to 3 in. The anodes are cast with a hole in the top and are suspended in muslin bags from the conducting supports by C-shaped hooks of gold. The cathodes are strips of silver rolled out to a thickness of $\frac{1}{16}$ in. and bent over at one end to hang from the supports.

The electrolyte is a 3 per cent solution of silver nitrate containing about 2 per cent of free nitric acid. It is kept uniform either by circulation effected by air lifts of hard rubber, forcing the solution from the bottom of the cell and discharging at the surface, or by gentle agitation furnished by glass propellers connected to a motor-driven line shaft.

The first step in the operation is the preparation of the bullion for refining, the making of anodes for the refining cells. While the process allows considerable latitude in the amount of gold in the anode, it is customary in practice, in order to secure more uniform conditions in the cells, to make up anodes having a definite ratio of gold to silver. The usual make-up is an alloy containing 300 to 350 parts of gold per 1000 with not over 100 to 150 parts of base produced by blending low-grade gold bullion, which cannot be handled directly by the Wohlwill process, with bullion in which the silver predominates. These silver anode melts of 4500 to 4800 troy oz. are melted in No. 100 graphite crucibles and cast into anodes of the desired shape and size. A tapering pin in the mold provides the hole in the anode used for suspension in the cell.

A current density of about 14 amp. per sq. ft. of cathode is maintained, using a voltage of 1 to 1.3. Under current action, the silver and base metals are dissolved at the anode, the gold and insoluble residues remaining in the muslin bag in a brittle brownish-black condition resembling a poor grade of lignite. This "black gold," as it is called, retains the original shape of the anode, and when removed from the cells it is broken up to remove "cores" of unparted bullion which it sometimes contains. After a thorough washing with hot water, the black gold is dried and melted into anodes for treatment by the Wohlwill process. The fineness of these anodes depends not only on the quality of silver anodes from which obtained, but also on the current density used in the parting operation and the condition of the electrolyte. The fineness ranges from 800 to 900 parts of gold with 50 to 100 parts of silver.

Pure silver is deposited on the cathodes in a crystalline form; this is scraped from the cathodes at intervals into porcelain jars. Crystals that fall to the bottom of the refining cells are periodically removed and added to the cathode production. The collected silver is thoroughly washed with hot water, in either porcelain filters or earthenware centrifugal machines. In the latter case, the silver is placed in an earthenware basket or rotor, lined with 7-oz. cotton duck, provided with a series of channels at its periphery for carrying off the wash water. This basket makes 800 r.p.m., and washing is effected very rapidly. After washing, the centrifugal is operated for a time, drying the silver sufficiently to be removed and charged into the

which protects them from further action, thus rendering them practically insoluble, and an evolution of chlorine results.

The gold deposited at the cathode is very hard and quite dense, and the starting sheet is melted with the deposited gold. The cathodes are removed after receiving

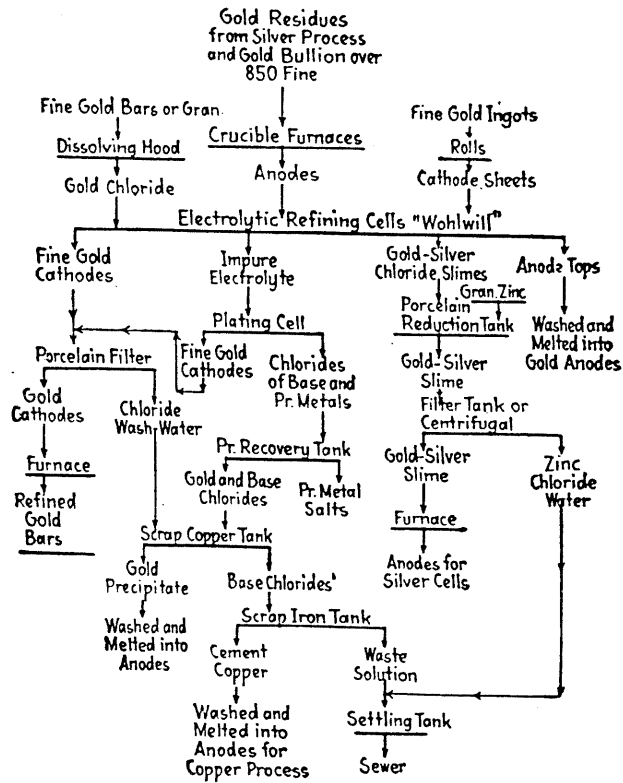


DIAGRAM 2.—Gold refinery flow sheet.

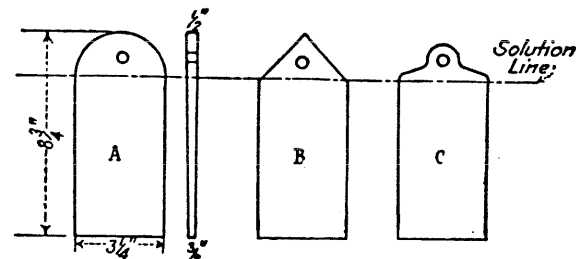


FIG. 3.—Anode types.

a deposit of 150 to 200 oz. of gold, washed in porcelain filters, dried, and melted without the use of fluxes in melts of 8000 to 9000 oz. and cast into bars having an average fineness of 999.5 to 999.8. Frequently, these melts will run to 999.9 in fineness.

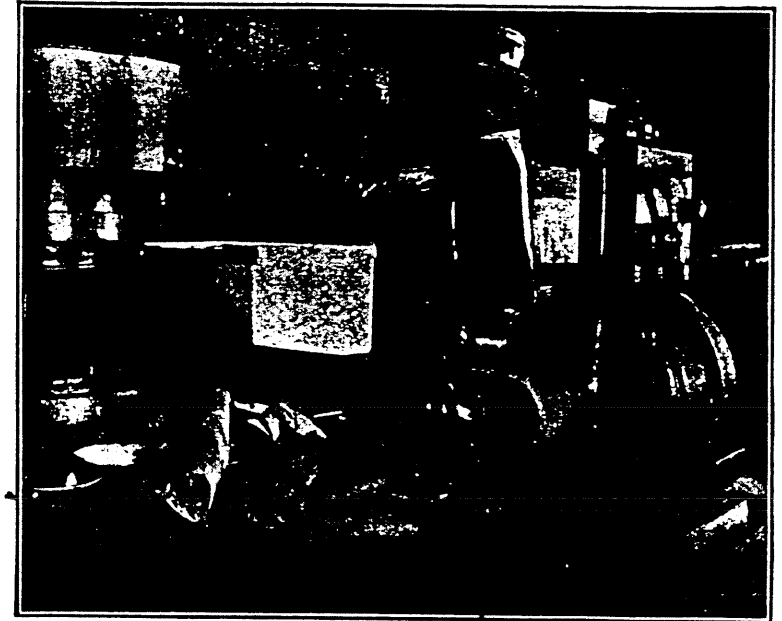


FIG. 4.—Motor-driven earthenware centrifugal for washing and drying slimes.



FIG. 5.—Wohlwill cells. Anode shown on left, cathode on right, thin rolled gold strips in foreground for starting sheets.

As the base metals are dissolved at the anode, the gold content of the electrolyte drops and it is necessary to add strong gold chloride at intervals. A rapid and fairly accurate method of testing the electrolyte is to precipitate the gold in 1 cc. with an excess of ferrous ammonium sulphate, and to determine the excess used by titrating back with potassium permanganate. The ferrous solution is prepared by dissolving 154 g. of the salt in 500 cc. of distilled water, adding 5 cc. of concentrated sulphuric acid and diluting to 1 l.; 1 cc. of this solution will precipitate 25 mg. of gold. The permanganate solution is made up so that 1 cc. will equal 1 cc. of the ferrous solution by dissolving 12.3 g. of the salt in 1 l. of distilled water.

In order to take care of the depletion of gold in the electrolyte, it is necessary to keep constantly on hand a stock of strong gold chloride. This chloride is made either by dissolving fine gold bars or granulations in aqua regia, or electrolytically, by passing a current through an electrolyte of concentrated hydrochloric acid, using anodes of fine gold and fine gold cathodes suspended in a porous porcelain cell. The porous cup prevents the deposition of the gold at the cathode, and the gold dissolved at the anode is retained in solution. In either method, the operation is carried on under a hood. The resultant gold chloride has a strength of 375 to 450 g. of gold per liter.

ut 5 per cent of the gold treated falls mechanically into the silver chloride

The reduction of the silver chloride is effected by use of granulated zinc in tanks, sufficient acid being present to start the action. After reduction is complete, the slimes are thoroughly washed in a filter or centrifugal machine and directly into anodes for the silver-refining cells. These slimes will average in 250 to 500 parts gold, 30 to 40 parts base, balance silver, and in the melting, 1 part gold or silver bullion is added as required to produce an alloy of the fineness desired by the silver-refining operations.

The gold in the spent electrolyte and wash waters is recovered by precipitation with ferrous sulphate or by scrap copper. As gold so recovered is in a very fine state of division and difficult to melt and wash without loss, an electrolytic recovery is preferred. This is accomplished by the use of a double-compartment cell in which the inner cell is placed in the center of a large cell. The inner cell is charged with concentrated hydrochloric acid, while the foul electrolyte is placed in the outer cell, and communication is made between the two solutions by a series of short glass siphons resting on the edge of the inner cell. The air is exhausted from these siphons, and the anions enter, thus permitting a flow of current through the electrolyte. Anodes of fine gold are suspended in the inner cell and gold strips in the outer cell. Under current action, gold chloride is formed in the inner compartment and the gold in the electrolyte is deposited on the cathodes. By regulation of the voltage, practically all the gold in the foul electrolyte may be plated out and the gold so obtained is used for the regular production of the cells. One or two of these plating cells will handle all the foul electrolyte from 48 of the small refining cells and at the same time add considerably to the stock of strong gold chloride.

As the government has no interest charges to consider on metal held in process, the noble metals are used for conductors, and the problem of securing good electrical contacts is in a measure eliminated.

A flow sheet (Diagram 2) shows the procedure in gold-refining operations.

All the foul solution from which the silver and gold have been recovered is pumped into large wooden tanks containing scrap iron, in which the copper is recovered as cement copper, and any gold, silver, or platinum metals that have escaped the previous operations are recovered. To recover the values in this cement copper, a small electrolytic copper plant is operated, producing pure copper and a sludge containing the precious metals. This sludge is a veritable dragnet of impurities, containing

Making
of
AuCl₃

besides Au, Ag, and Pt, the base metals Cu, As, Sb, Pb, Bi, etc. This is usually handled in small amounts in silver-anode melts and the precious metals recovered from the regular process.

Platinum Metals Recovery.—The procedure for the recovery of the platinum metals in the government refineries is as follows:

The foul electrolyte from the gold-refining cells is allowed to cool, thereby permitting the salts of silver and lead to settle. The clear solution is siphoned off, ammonium chloride is added with thorough stirring, and the yellow ammonium chloroplatinate is precipitated. After the platinum salt has settled, the solution is transferred to a stoneware tank for the recovery of palladium.

This solution is electrolyzed, using an insoluble carbon anode and a refined gold sheet as the cathode. Under current action, chlorine is evolved at the anode and a flesh-colored salt of palladium is formed which settles to the bottom of the cell while the gold is deposited in a pure state at the cathode. The current during this operation is gradually reduced as the gold in solution becomes depleted in order to keep the gold deposit hard and prevent contamination of the palladium salt. The range of current density is 20 amp. to 2 amp. per sq. ft. of cathode surface. The electrodes are spaced 2½ to 4 in. apart. The deposited gold is added to the gold-cell production, while the gold remaining in the electrolyte is recovered by cementation on copper slabs. The remaining solution finds its way to wooden tanks where copper and traces of the precious metals are recovered by cementation on scrap iron.

The platinum and palladium salts are washed with a cold saturated solution of ammonium chloride and dried. The palladium is very soluble, and great care should be exercised in the washing; the ammonium chloride should be freshly chlorinated, and only the bulk of the gold and copper chloride should be removed.

Iridium is recovered from the iron skimmed from certain melts. These skimmings are granulated and dissolved in hydrochloric acid to remove the iron. Further treatment of the residues is necessary depending on the metals present before using the usual peroxide fusion for recovery of the iridium. Crystals of osmiridium may be recovered directly in the gold-refining cells.

Platinum Metals Refining.—Practically all the refining and melting of the platinum metals is performed at the United States Assay Office in New York.

The usual procedure in refining crude platinum sponge is to redissolve in aqua regia, evaporate the solution to dryness to expel the nitric acid, dissolve the residue in water, and reprecipitate the platinum with ammonium chloride. In large-scale operations, this is a long and tedious process, so the government refineries have developed an electrolytic method to effect a solution of the crude sponge.

The crude sponge is placed in perforated stoneware cells or baskets that are suspended from the electrode support in an electrolyte of hydrochloric acid, contact being made by a heavy platinum strip fastened to the bus bar and penetrating the sponge. The cathodes are thin platinum sheets suspended from heavy platinum-wire conductors in porous cells of the same size and shape as the perforated anode basket. The electrolytic action dissolves the sponge at the anode, while the porous cup prevents the deposition of the dissolved platinum at the cathode. An alternate scheme, which also gives satisfactory results, is one in which a platinum sheet is placed on the bottom of the electrolytic cell, the crude sponge is placed on this sheet as the anode, and the porous cups in which are the platinum strips are placed at the ends of the cell. Air is used for agitation of the electrolyte. This solution from the crude sponge is evaporated on steam coils to remove excess acid, and filtered and ferrous sulphate is added to remove the gold. The solution is carefully filtered again and the platinum again precipitated with ammonium chloride. This precipitate should be freed from the filtrate as soon as possible and washed until free of iron. The platinum salt is

of

Pt

Add Alcohol

Peroxide Fusion

dried and reduced to sponge by gentle heating in a clay crucible. The refining is carried on in batches of 1000 to 2000 troy oz., and the crude sponge can be raised from 80 per cent to 99½ per cent in one treatment as outlined.

The crude red salt of palladium, after washing, is treated with ammonium hydroxide until no more is dissolved, and after filtering, the yellow dichlorodiamine palladium is precipitated by cautiously adding hydrochloric acid until no more of the yellow salt forms. During this precipitation, great care must be exercised to prevent overheating, and an excess of acid should be avoided. This yellow salt is drained, washed, and redissolved with ammonium hydroxide and again precipitated with hydrochloric acid. It is then carefully washed on a filter, dried, and sponged in clay crucibles. This sponge is ground and reduced by soaking in alcohol and bringing to a red heat in a carbon or graphite crucible fitted with a tight cover. This sponge must be allowed to cool in the crucible. Palladium having a purity of 99 to 99.75 per cent results.

An Ajax-Northrop induction furnace is used in the melting of the platinum and palladium sponge, using a specially designed zirconium-oxide crucible. Due to the high temperature and the thorough mixing action afforded by the induction furnace, the metal is considerably better for spinning than when melted by the torch method.

An excellent treatise on the purification of the platinum metals is furnished by Edward Wichers, Raleigh Gilchrist, and William Swanger.¹ Further notes on the treatment of the platinum metals will be found in the last chapter, Minor and Rare Metals.

¹ *A.I.M.M.E. Tech. Bull. No. 87, March, 1928.*

CHAPTER XI

HYDROMETALLURGY OF GOLD AND SILVER¹

Occurrence of Gold.—Native gold is invariably alloyed with more or less silver, but it is exceptional to find any other metal in the alloy. It is found in veins associated with quartz and various sulphides—notably pyrite, pyrrhotite, galena, chalcopyrite, arsenopyrite, less commonly blende; sometimes with carbonates, especially ankerite; and small proportions of tellurides of lead and bismuth. Sometimes the metal is finely disseminated through such sulphides, sometimes deposited on the surface of the mineral particles in fairly large grains. One particular sulphide, *e.g.*, chalcopyrite, may monopolize the gold. In the oxidized portions of veins the gold is often associated with limonite, and gold-bearing quartz often contains small proportions of copper carbonates and manganese oxides. Electrum, containing 35 per cent or more silver, is found only in the vicinity of silver mines. When gold is found apparently disseminated in igneous or metamorphic rocks, minute veinlets of quartz or carbonate usually accompany it.

Gold telluride, usually containing silver and sometimes mercury telluride, occurs in veins of quartz and carbonate; when oxidized, the resulting native gold is often extremely pure and finely divided and may be coated with tellurous oxide (mustard gold).

The gold of placers or creek and river gravels is found occasionally in nuggets of large size, but more commonly in small grains, often water-worn; in some deposits a considerable proportion of the grains pass a 200-mesh sieve. The silver content averages less than in vein gold, and it is, as a rule, easy to amalgamate. That from buried river gravels is similar, but often coated with oxide or sulphide of iron. The gold of sea beaches is usually finely divided or in thin scales.

For metallurgical purposes gold has been roughly classified as "free" or amalgamable and "refractory"; "float gold" is fine and in a condition making it easily floatable on water—the telluride is also easily floated—"rusty gold" is coated with some mineral that retards amalgamation (usually oxide of iron, manganese, or tellurium); "encased gold" is completely enveloped in grains of quartz or other mineral and requires finer crushing to liberate it.

Among the minerals sometimes mistaken for gold may be mentioned pyrite and marcasite, and especially chalcopyrite. Grains of the latter, in polished faces of ore, often closely resemble gold in color and luster. Thin flakes of biotite and other micas, especially when partly oxidized, and other micaceous minerals, such as hematite and limonite, may also imitate it closely.

In panning or concentrating, many people have been misled by heavy lead minerals of a yellow color, such as the molybdate, chromate, tungstate, and even the phosphate, but these are distinguishable under a lens or low-power microscope by their brittleness and transparency. Some of the numerous basic sulphates of iron are at times difficult to distinguish from gold when exposed on freshly fractured vein stuff. Particles of natural or artificial litharge, brass, or "spelter solder," and even superficially oxidized lead alloys, sometimes bear an astonishing resemblance to gold. These, and specks of native copper or copper from blasting caps, may find their way into mine samples or drillings and be found in panning.

¹ A revision by the editor, in 1944, of the chapter contributed to the first edition by W. J. Sharwood.

On the other hand, mustard gold, resulting from oxidation of telluride, may have a distinctly earthy luster, and gold of low fineness may be easily overlooked.

Native silver and the chloride characterize the oxidized zone of most deposits. Native silver, usually nearly pure, occurs in very fine particles, threads, etc., and sometimes in masses which may reach several thousand pounds weight. In the Michigan copper mines, pure silver and pure copper occur attached and intergrown. Some native silver contains a little mercury. Coarse lumps are best hand picked, but the smaller are concentrated, or amalgamated, and the fines cyanided.

The chloride (AgCl) is readily reduced to metal by contact with metallic Fe, Zn, Al, or even Cu in contact with an electrolyte, and is then easily amalgamated by mercury. Alkaline cyanide, or thiosulphate solution, dissolves it readily, and also silver bromide and iodide, which often accompany it; strong solutions of chlorides have less solvent action.

The sulphide (Ag₂S) dissolves in strong cyanide solution, but not in chlorides or thiosulphates. It is slowly amalgamated by mercury when in contact with an electrolyte, and the action is facilitated by thiosulphates and copper salts, especially in the presence of metallic iron, etc. When roasted it yields Ag₂SO₄, which is somewhat soluble in water.

copy of The numerous complex sulphur-arsenic and sulphur-antimony compounds of silver are not so readily amalgamated unless roasted; they are decomposed by grinding with metallic aluminum and sodium hydroxide or carbonate.

Galena often contains silver in the form of sulphide; and the selenide (Ag₂Se) and occasionally the telluride (Ag₂Te) occur in small amounts in some gold and silver ores, and apparently in some copper deposits.

Gold and Silver Alloys.—Pure gold is distinctly softer than silver; either is hardened by the addition of a small proportion of the other, or of copper or other base metal. In gold-silver alloys the maximum hardness occurs with about one-third silver. Small additions of silver reduce the gold color materially, but affect the melting point very little up to about one-third silver. Electrum is gold, especially the native metal, containing 15 to 45 per cent silver, rendering it pale. Green gold is a similar alloy containing about 10 per cent silver. The red-gold alloys contain copper.

Jewelers' gold usually ranges from 18 (Au 750) to 10 k. (Au 416) and frequently contains both copper and silver as alloy. The lower grades often contain some zinc, which helps to counteract the redness due to copper. They are sometimes made by alloying brass with gold, but extreme care is necessary to avoid certain impurities in the brass or copper used, especially lead or arsenic, which cause brittleness. British gold coin is 22 k. (Au 916.6), but alloys as low as 9 k. (Au 375) are recognized and hallmarked in England.

The proportions of copper and silver are determined by the color of the gold desired. Thus in 18-carat gold, 10½ per cent Ag and 14½ per cent Cu gives a dark tone; while 14½ per cent Ag and 10½ per cent Cu gives a light tone to the alloy. The compositions in the tables on page 291 are approximately correct.

White gold is properly an alloy of gold with palladium; if legitimately stamped 18 k., it will contain 18 parts gold (Au 750) and the remaining 6 parts are palladium, with usually a little silver. This alloy has a pure-white color and a high melting point. Palau and rhotanium are similar. A cheap imitation is produced by melting gold with a nickel alloy. The mixture sold for producing "white gold" by adding it to fine gold is Cu, 55 per cent; Zn, 21 per cent; and Ni, 24 per cent. A similar mixture for producing "green gold" is merely brass: Cu, 67 per cent, and Zn, 33 per cent.

For soldering gold there are many recipes, the aim being to produce an alloy considerably more fusible than that of which the object is made, but not differing much in color. Many of these soldering alloys contain a considerable proportion of zinc

with copper, silver, and gold; with copper, a considerable percentage of zinc does not cause brittleness, though the alloys are often extremely hard and difficult to roll. In recent formulas, cadmium is substituted for zinc. Such solders lose zinc (or cadmium) by volatilization when heated, becoming gradually less fusible.

Carat	Fineness	Per cent			
		Au	Ag	Cu	
24	1000	100			English standard Metric standard
22	916	91.66	4.16	4.16	
..	900	90	5	5	Dark Light
20	833	83.3	8.3	8.3	
18	750	75	10.4	14.6	
18	750	75	14.6	10.4	
14	583	58.3	25.0	16.6	
14	583	58.33	4.16	37.5	
10	416	41.6	16.6	41.6	Solder Solder
..	62.5	22.5	13.0	
..	54.5	31.75	13.75	

The silver alloys are used for coinage, plate, solders, etc.

	Per cent			
	Ag	Cu	Zn	
Sterling silver.....	92.5	7.5		Melting point 778°C.
Rupee silver.....	91.6	8.3		
Standard silver.....	90.0	10.0		
Solder:				
Hard.....	80.0	13.2	6.8	
Medium.....	75	20	5.0	
Pure silver.....	72	28	
Plate.....	64.5	22.5	13.0	
Chain.....	62.5	31.25	6.25	
Quick.....	57	27.5	11.5	
Bureau of Standards.	40	14	6	Sn 4 per cent. For resoldering Sn 40 per cent. Melting point 400°C.

Aluminum forms a number of alloys with gold; one of these (AuAl₂, 22 per cent Al) has a remarkable purple color. The so-called aluminum gold is an alloy of copper with about 25 per cent Al, very slightly attacked by nitric acid, and closely resembling gold in color, but of low specific gravity. *Purple color*

Pure silver when melted absorbs oxygen from the air (up to twenty-two times its own volume) unless air is displaced by some other gas or the fused metal covered with borax, salt, or charcoal. On cooling to near solidification this oxygen is given off suddenly, the surface of metal sprouting or spitting. Small proportions of foreign metals usually prevent this. The oxygen is probably retained by fused metal as a suboxide, like that held by copper after solidification. Gold does not absorb oxygen.

When gold or silver containing a small percentage of lead is heated, or is kept just below solidifying point, a eutectic rich in lead exudes or liquefies out; this often oxidizes, producing a peculiar "vegetation" on the surface. This is due to formation

of PbO mixed with minute globules of gold (or silver). In extreme cases the entire alloy may form a soft cauliflower-like mass.

The small proportion of silver alloyed with native gold and mill bullion is of some economic importance, usually more than covering cost of marketing refined bars. Assuming silver at 50 cents per oz., the per cent of gross value due to silver is as follows:

Ratio		Percentage, silver value
Gold	Silver	
900	100	0.16
800	200	0.32
700	300	0.60
600	400	0.95
500	500	1.43

With silver at \$1 per oz., these figures would be nearly doubled, and for other values nearly proportional.

A minute proportion of lead—less than 1 part in 1000—makes gold brittle, especially when hot. This seems to be due to a highly fusible eutectic, which can be seen between the crystals of pure metal in a polished and etched section. Similar effects are produced by Bi, Te, Sn, Sb, As; while Zn and Cd in fair proportions yield less brittle alloys. Annealing removes brittleness due to traces of Pb, not that due to Bi or Te. Silver is similarly affected by most of these elements.

Tellurium renders gold extremely fusible; on heating in air the tellurium is slowly volatilized or oxidized, leaving bright globules of gold still retaining some tellurium.

Gold combines or alloys readily with tellurium, and with fusible metals generally, forming fusible alloys; it is not attacked by the vapor of selenium or sulphur. Silver is at once attacked when heated in the vapor of S, Se, or Te, forming Ag₂S, Ag₂Se, or Ag₂Te; like gold it alloys readily with fusible metals.

Gold resists all single acids, but is readily attacked by aqua regia; the most effective proportions are 1 part nitric to about 4 parts strong hydrochloric acid; any mixture of hydrochloric acid with a nitrate, nitric acid with a soluble chloride, or sulphuric acid with a nitrate and a chloride similarly attack it. It is very slowly acted upon by hot solution of ferric chloride. Moist chlorine gas converts gold into AuCl₃. Silver combines superficially with Cl, the AgCl then protecting the metal unless removed by some solvent. For this reason Au-Ag alloys are not dissolved completely by aqua regia unless the AgCl is removed from time to time from the surface by scouring or by some solvent, such as ammonia, cyanide, or hyposulphite.

Gold-chloride solutions (AuCl₃, HAuCl₄, NaAuCl₄, and other chloraurates) are reduced to metal if evaporated and gently heated, and are also reduced to metal by nearly all reducing agents such as base metals generally, SO₂ and salts of Fe⁺ and Sn⁺. Silver is readily dissolved by nitric or hot sulphuric acid, NO or SO₂ being evolved, but resists most others. Silver nitrate, sulphate, and chloride are not readily decomposed but may be heated without decomposition; they are easily reduced to metal by contact with base metals, Zn, Fe, Cu, etc.

Parting.—The cupellation of lead removes it as oxide, together with other base metals, leaving gold and silver. Silver-bearing lead may be enriched by the Pattinson process, in which crystals of pure lead are removed, leaving the more fusible eutectic, the process being carried on in stages and the enriched lead finally cupeled. Silver

and gold may be more readily removed from lead by the Parkes process, in which a small percentage of zinc is added which, on cooling, crystallizes and rises (zinc being insoluble in solid lead), carrying up the precious metals as a crust, which is removed and refined.¹

Gold and silver are separated or parted by means of nitric acid, NO being given off and AgNO₃ formed. This requires the ratio Ag: Au to be at least 2:1, though 3:1 was formerly preferred. Hot sulphuric acid also dissolves silver away from gold if the proportion of silver is large enough, SO₂ being evolved. Gold containing relatively little silver must have silver (or in some cases base metal may be used) added to reduce the gold to such a proportion that it will not protect the silver from attack.

It is preferable to use the Wohlwill process, electrolyzing the gold in a solution of HAuCl₄ + HCl, with gold cathodes, an alternating current being sometimes superposed upon the high-density direct current used. Silver remains insoluble as AgCl.

Silver containing but little gold is electrolyzed in a slightly acid solution of silver nitrate, with a silver or carbon cathode, leaving gold insoluble; this is used in the Moebius and Balbach-Thum processes.

The following tabulated data are of value in connection with the refining of gold and silver:

	Gold	Silver	Copper
Melting point, degrees centigrade.....	1063	961	1083
Specific gravity.....	19.3	10.5	8.95
Specific volume (cubic centimeters per gram)....	0.0518	0.0952	0.1117
Cubic inches for 1,000 troy oz. = 1,898/sp. gr. ...	98.3	180.8	212
Cubic inches for 100 lb. avoird. = 2,770/sp. gr. ...	143.5	263.8	309.5

In an alloy containing *G* per cent gold, *C* per cent Cu, and *S* per cent Ag, the specific gravity is very closely

$$\frac{100}{0.0518G + 0.0952S + 0.1117C}$$

Cementation is an ancient method of freeing gold from silver and base metals. The metal was first granulated by pouring into water, or beaten into thin plates. It was then placed in crucibles with a large proportion of aluminous earth and heated; silver, etc., was slowly oxidized (or possibly converted into sulphate or sulphide) and absorbed. Most recipes, however, include common salt and burned clay or powdered brick, tile, etc. When heated in contact with these, silver chloride is formed, fused, and absorbed. Gold treated several times in this way ("seven times tried in the fire") was rendered nearly pure.

Sulphur or pyrite was also used; heated in sulphur vapor, most of the silver and copper form Ag₂S and Cu₂S, which can be mechanically removed.

In *Guss and Fluss* parting, an alloy, containing at least 50 per cent gold, was heated in a crucible with 3 parts antimony sulphide, and poured into a mold; the gold, alloyed with antimony, etc., is found at the bottom and easily separated from the layer of "plachmal" above it. This gold alloy was then fused with 2 parts antimony sulphide, and the product again with 1 part. The process was repeated if necessary until

¹ See pp. 201 to 208.

enough silver had been removed, when the gold was finally melted with borax and the alloyed antimony oxidized by a blast of air.

In the sulphur-litharge process (*Pfannenschmied*) a granulated alloy, rich in silver, was heated with sulphur, yielding Ag_2S , in which gold is disseminated. To collect the gold, a small percentage of litharge was added, yielding a fusible lead-silver alloy, which carried down most of the gold; a second or third treatment removed practically all the gold. Metallic iron was sometimes used instead of litharge to reduce a portion of the silver and collect the gold. Reduction of the remaining sulphide yielded a fairly pure silver.

Gold bullion, rendered brittle by Te, Bi, Pb, etc., may be softened by throwing a little HgCl_2 on the fused metal, also by adding solid AgCl or Ag_2SO_4 , by stirring with Cl gas or an air blast; stirring with NaHSO_4 , NaNO_3 , or MnO_2 is also effective. More or less silver may be removed by these methods, especially by Cl or NaHSO_4 .

Recovery of Gold and Silver.—All gold and silver ores yield a high percentage of their precious metal when smelted with lead or copper ores, and an almost complete saving of them is effected in refining the lead and copper recovered. A large proportion of the silver of the world, and a considerable amount of the gold, is thus obtained as a virtual by-product from the smelting and refining of lead and copper ores, including some zinc-lead and zinc-copper ore. Some of this precious metal comes from concentrate, some from siliceous ore used as flux; comparatively little true gold or silver ore is directly sold for smelting. Smelting charges and deductions on the full weight of ore, with the cost of freight and loading, often make it advisable to adopt some method that may be far inferior metallurgically, as regards percentage recovery, but that puts the precious metal in a form in which it is more readily salable, such as bullion or rich precipitate.

Outside of smelting and refining, the present-day metallurgy of gold and silver may be summarized under three heads: mechanical methods (concentration, flotation, and blanketing, etc.), amalgamation, and the cyanide process. Chlorination of gold and hyposulphite leaching of silver ores were practically superseded by cyaniding by the year 1900; chloride volatilization and other promising processes have not yet assumed commercial importance. The products of concentration and flotation may be either smelted with lead or copper ore, or may themselves be treated by amalgamation or cyanidation. Each of the latter processes consists of five essential steps.

Amalgamation:

Comminution of ore.

Bringing ore in contact with mercury (and with chemicals in the case of silver minerals).

Separating amalgam.

Retorting amalgam to remove and recover mercury.

Melting and refining the crude bullion from the retort.

Cyanidation:

Comminution of ore (often combined with auxiliary processes of amalgamation, concentration, or classification, neutralization, or washing out soluble salts).

Dissolving gold and silver.

Separation of solution from ore, and washing residue.

Precipitating gold and silver from solution.

Refining precipitate and melting bullion.

The treatment of placer deposits is a special case of concentration, often combined with amalgamation.

PERCENTAGES PRODUCED BY DIFFERENT PROCESSES IN THE UNITED STATES
(*Mineral Resources, U. S. Bureau of Mines Yearbook, 1940.*)

	Gold					Silver				
	1936	1937	1938	1939	1940	1936	1937	1938	1939	1940
Placers, mainly dredging.....	23.9	24.6	27.9	28.6	31.0	0.2	0.2	0.2	0.3	0.3
Amalgamation.....	27.1	25.3	23.1	21.1	19.7	0.7	0.5	0.4	0.4	0.3
Cyanidation.....	18.8	19.3	22.6	22.3	21.4	4.1	4.3	7.0	7.1	7.5
Smelting ore and concentrate....	30.2	30.8	26.4	28.6	27.9	95.0	95.0	92.4	92.2	91.9

In South Africa about 65 per cent of the recovery is by amalgamation, 35 per cent by cyanidation; on the Mysore Field, India, nearly 90 per cent by amalgamation.

PERCENTAGES BY WEIGHT FROM VARIOUS SOURCES IN THE UNITED STATES

	Placers	Dry or siliceous ores	Copper ores	Lead ores	Zinc ores	Copper-lead and copper-zinc ore	Lead-zinc ores	Total ounces
Gold.								
1906....	28.24	63.17	5.77	1.29	0.02	1.26	0.25	4,703,000
1907....	28.22	62.11	6.44	2.56	0.14	0.05	0.48	4,227,500
1914....	25.30	66.56	6.00	1.69	0.04	0.01	0.40	4,418,000
1915....	22.66	67.57	7.22	1.78	0.10	0.05	0.62	4,754,500
1920....	25.3	63.93	7.18	1.96	0.15	0.16	1.32	2,383,000
1921....	28.89	66.02	2.25	2.64	0.003	0.007	0.19	2,345,000
1940....	31.0	55.5	11.2	0.36	0.003	2.00		4,869,949
Silver:								
1906....	0.30	29.27	27.69	26.72	0.17	11.88	3.97	57,362,450
1907....	0.24	36.27	26.58	32.99	0.18	0.93	2.81	52,497,060
1914....	0.22	39.95	21.30	27.72	0.21	0.36	10.24	69,623,200
1915....	0.21	35.53	25.96	27.40	1.57	0.33	9.00	72,353,700
1920....	0.13	36.22	21.49	30.19	2.23	1.18	8.56	56,536,900
1921....	0.18	51.88	10.36	32.30	0.01	0.97	4.30	46,171,300
1940....	0.28	40.5	29.0	4.4	0.03	24.2		70,549,362

The commercial ratio between the values per ounce of gold and silver was about 15 to 16 from 1800 to 1873; since 1873, the annual average has ranged from 18 to nearly 40. One of the largest producers turns out about a ton of silver per day; one of the largest gold mines has for years yielded a ton of fine gold per month; the value of the silver is much less than that of the gold.

To generalize roughly, a gold deposit, under extremely favorable conditions, may be profitably dredged when containing only 1 part in 10 millions, or 11 cents per ton; 1 part in a million assures a reasonable profit in a placer. A gold ore containing 10 parts per million (\$11 per ton), while of low grade, is assuredly profitable if not too small or unfavorably situated; and half or even one-third of this value may be payable if very large and otherwise advantageously situated. Silver ores begin to be of commercial importance when containing about 100 parts per million, or 3 oz. per ton.

When associated with commercial ores of copper and lead, they are extractable at negligible cost and in such cases smelters usually pay for over 0.025 oz. Au or 1 oz. Ag.

WORLD PRODUCTION OF GOLD AND SILVER, 1939
Reported by U. S. Bureau of Mines and Director of the Mint

Source	Gold, oz.	Silver, oz.
United States.....	5,559,139	57,808,000
Canada and Newfoundland.....	5,114,692	24,584,689
Mexico and Central America.....	1,017,623	80,668,824
North America.....	11,691,454	163,061,513
South America.....	1,775,661	31,551,087
Europe.....	5,644,143	21,861,870
Asia.....	2,657,687	22,386,996
Africa.....	15,510,377	4,618,209
Oceania.....	2,210,346	14,621,894
Total.....	39,489,668	258,101,269
Total United States production 1792-1940.....	262,487,295	3,650,909,393

Gold in Sea Water.—Gold and silver have long been known to exist in the waters of the ocean, and occasional projects are brought forward to recover the gold. The statement of Sonstadt that the gold in sea water is "less than 1 grain per ton" is often interpreted as meaning at least 1 gr. The actual average is probably less than $\frac{1}{40}$ grain or $\frac{1}{40}$ cent per ton, and entirely below the present economic limit for extraction. Even at this low estimate, the aggregate amount in the ocean (estimating the ocean at about 320,000,000 cu. miles, each of 4,600,000,000 tons of water) is enormous.

METALLURGICAL SYSTEMS

Most of the modern metallurgical schemes for gold and silver ores are covered by the following outline:

1. Preliminary breaking by crushers of jaw or gyratory type.

2. Crushing:

Dry:

By rolls or disks (with or without screens to return oversize).

Wet:

Stamps alone.

Stamps

followed by.....

Ball mills or rod mills

followed by.....

Heavy stamps with coarse screens

chileans, ball mills, or rod mills

} pebble mills.

The rotary mills are generally run in closed circuit with classifiers.

Dry crushing:

Followed by cyaniding (with or without preliminary water or alkaline wash)

Wet crushing:

In water (with or without amalgamation or concentration) Draining or dewatering } Cyaniding.

In cyanide solution with or without amalgamation or concentration.

With special reagents followed by cyaniding (such reagents as H_2SO_4 , SO_2 , or aeration in presence of lime).

3. Treatment of crushed product:

Straight cyanidation (with or without prior amalgamation), and either without roasting or after roasting to destroy carbonaceous matter or sulphur compounds. Concentration (with or without amalgamation) by tables, vanners, corduroy blankets, canvas, or flotation.

Concentrate:

Smelted, or sold to smelter.

Cyanided (intensively), raw or after roasting.

Amalgamated, then cyanided.

Tailing:

Discarded, if crushed in water and low grade.

Cyanided.

In case of cyanidation of original product or of tailing there is:

Classification into sand and slime (with or without partial regrinding).

Sand:

Leached with cyanide solution.

Slime:

Discarded, if crushed in water and low grade.

Cyanided, by agitation or in filter press.

All-sliming:

Cyanided, by agitation or in filter press.

4. Separation of cyanide solution from ore or tailing:

Filtration:

Gravity (sometimes aided by vacuum) for coarser leached products.

Vacuum or pressure (in basket filters for fine products, intermittent).

Vacuum with rotary filters (continuous) sometimes in series.

Pressure in filter presses (intermittent).

Decantation:

Intermittent, after settling.

Continuous, with intermittent or continuous final filtration.

Continuous countercurrent, with thickeners in series, with or without final filtration.

5. Precipitation of gold and silver from cyanide solution (preferably deaerated by vacuum treatment, and clarified if necessary):

Zinc shaving in boxes with compartments for upward flow.

Zinc dust in filter presses.

Aluminum dust in filter presses.

6. Refining precipitate:

Preliminary acid treatment for removal of zinc, etc. (often omitted), or calcination.

Direct fusion with fluxes in crucibles or on hearth.

Lead refining: briquetting or mixing with a litharge-borax flux, fusing on reverberatory hearth or in blast furnace, followed by cupellation of rich-lead bullion.

Treatment of by-products usually necessary.

Generally, removal of free gold at an early stage of treatment tends to minimize the dissolved gold discharged with residue or tailing. On the other hand, in "all-sliming" the cyanide process is simplified by omitting amalgamation. If coarse gold is not amalgamated, it must be removed by mechanical methods or ground sufficiently fine to ensure rapid dissolution. Some Canadian plants are giving a bulk flotation to the cyanide tailings in a circuit rendered somewhat acid with SO_2 . The

concentrate is roasted to produce further SO_2 , and then cyanided. The process is said to yield a profit on a 30 cent tailing.¹

MECHANICAL TREATMENT*

Mechanical Separation

Alluvial Concentration.—In handling alluvial material the main problem is to get rid, at the first opportunity, of most of the boulders and coarse gravel, without losing any of the gold originally adhering to them, and to disintegrate rapidly and completely any lumps of sticky clay that would carry fine gold further down the sluices or even into the tailing. It is not generally desirable to crush any of the pebbles.

In hydraulic work the coarse gravel running down the sluices does much of the work of disintegration, and the coarser portion is removed when desired by means of "under-currents" or grizzlies of steep grade, which allow the finer material to pass through and conduct it to boxes or tables where conditions are more favorable for settling. After passing over the grizzly, the coarse gravel may be discarded or returned to the main stream.

A revolving trommel with lifters, and furnished with ample water sprays, is an ideal device for performing these operations on a large scale, and is now standard practice for dredges, the pebbles acting as disintegrators. By graduating the diameters of the holes to suit the material handled, a comparatively uniform discharge may be obtained throughout the length of a trommel, but by far the largest part of the gold passes the holes near the inlet end. Shaking screens have been used but consume too much power. One of the older "cement mills" for hard gravel was virtually a large trommel built of railroad or T iron. Another cement gravel mill is a pan with a stout vertical shaft carrying agitating arms, and fed with water, accumulated coarse rock being discharged at intervals by opening a door in the side or bottom.

In small operations, the same results are achieved by using a rocker with punched screen, fed a few pounds at a time; or by shoveling into a sluice box, at the head of which is a screen or set of bars, over which the material may be manipulated by a sluice fork or shovel.

The length of wooden sluice boxes is standardized at 12 ft., and a grade of 6 in. means 6 in. per box, or about 4 per cent, the width varying with the load. For small, semiportable boxes, the upper end of the bottom is sawed 2 or 3 in. wider than the lower end, so that they fit closely one in the other.

In large hydraulic work, boulders of several tons weight may enter the sluices and must either be carried through or blasted or lifted out; such sluices require stout linings of wood or steel.

Various types of riffle material have been used: cross-grain pine blocks, roughly squared, or flat-lying blocks up to 4 × 6 in., either form being separated by small strips of wood or bits of rock; boulders or roughly squared rocks; peeled pine poles; planks mortised or bored, or iron blocks cast with channels or pockets, and railroad steel.

Hungarian riffles are strips of wood from about 1 to 1.5 in. square up to 2 × 4 in. laid crosswise with about equal spacing; they are often undercut on the downstream side, and have tops sloping upward. When subject to heavy wear, they are covered with strips of iron or steel, manganese steel being most durable. By attaching them to longitudinal strips they form frames readily removed. A similar riffle for dredges is built of 1¼- or 1½-in. angle steel riveted to 6-ft. strips of the same material; the

¹ *Mining M.*, February, 1941, p. 72.

* Also see Concentration, p. 134, in the first volume, entitled "Principles and Processes."

angles are opened about 10 or 15 deg. above a right angle and point downstream. Another effective sluice lining is coconut matting covered with expanded metal (steel lath).

A special study of riffles for heavy work was made by P. Bouery at La Grange, who successfully used 40-lb. steel rails on 5-in. centers, resting on 2 × 6 in. pine strips set edgewise with spacers. He recommends invariably placing riffles crosswise. A riffle of manganese steel designed by Bouery for severe hydraulic work consists of riffle proper, spacers, and lockers; when worn, these can be used as liners.

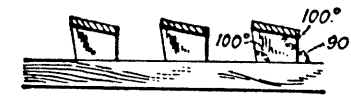


FIG. 1.—Hungarian riffles.



FIG. 2.—Bouery steel-rail riffle at La Grange.

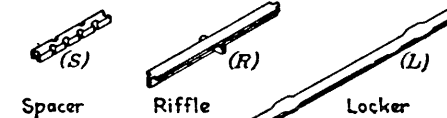
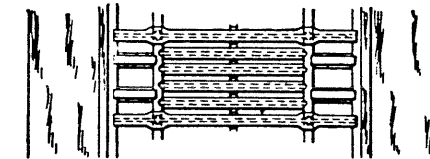


FIG. 3.—Bouery patent manganese steel riffle.

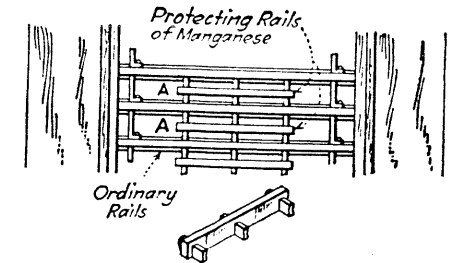


FIG. 4.—Railroad rail riffle with manganese protecting rails, at La Grange.

In cleaning up a sluice, clear water is run for some time; then, beginning at the head, the riffles are removed section by section, the dirt washed off, and the deposited gold washed down to the next section, where it can be scooped up into buckets. It is then taken to a point where it can be panned or treated in a rocker or special sluice to concentrate the gold further, and separate it from the accompanying black sand.

DISTRIBUTION OF GOLD IN SELECTED SLUICES AT LA GRANGE (P. Bouery)
(Boxes 1 to 4 were filled with pebbles, etc.)

Box number	Ounces of gold						Total ounces per 12-ft. box
	+10 mesh	+50 mesh	+100 mesh	+150 mesh	+200 mesh	-200 mesh	
5	45.8	50.7	1.38	0.36	0.31	1.45	100
6-16	18.0	83.3	2.33	1.00	0.31	0.83	43-108
22	1.73	20.22	3.08	0.70	0.25	0.62	26.2
48	0.18	2.18	1.06	0.12	0.05	0.16	4.15
88	0.018	0.12	0.47	0.008	0.026	0.005	0.65
136	0	0.053	0.027	0.043	0.011	0.01	0.14

Dredges.—The dredges now in general use have close-connected buckets of 5 to 15 cu. ft. capacity and are built of steel or wood, digging to a depth of over 80 ft. below the surface of the pond or stream in which they float.

The buckets discharge into a long revolving screen or trommel running at a grade of 5 to 10 per cent toward the stern, where the coarse material passes to the stacker, while the finer portion goes to the gold-saving sluices and may then be run out directly or may go to a second stacker. The land is usually left in a valueless condition, but resoiling is possible by the use of multiple stackers.

The screen may be cylindrical or stepped in diameter; it should have a baffle at the end of each section and must be well braced. In a large dredge it may be 10 ft. in diameter by 50 ft. or more, with a peripheral speed of 150 ft. per min. The perforations should be adapted to the material handled; one example has openings $\frac{3}{8}$ in. at the upper end increasing to $\frac{3}{4}$ in. at the discharge, another $\frac{1}{4}$ in. increasing to $1\frac{1}{4}$ in. The stacker belt may be up to 4 ft. wide, of eight-ply rubber, and will normally last a year or more. An internal spray pipe runs the full length of the screen, and two or more smaller ones outside; these must have an ample supply of water to wash the gravel and carry the fines over the sluices.

The sluices may be in one series or in two decks 4 or 5 ft. apart. They are usually about 30 in. wide, running crosswise of the deck at a slope of $1\frac{1}{4}$ to $1\frac{1}{2}$ in. per ft. (10 or 12 per cent) and then turning aft. Much the largest portion of the gold is caught in the first few feet of sluices; Janin mentions a 6-ft. dredge with 1457 sq. ft. of sluice area, catching 89 per cent of the total recovery in 292 sq. ft., or one-fifth of the total area. For more clayey material the area was increased to 3900 sq. ft. One 15-ft. dredge had 8000 sq. ft. of sluices in two decks; in another case 4500 sq. ft. in two decks was found needlessly large for a 15-ft. dredge digging 600 cu. yd. per hr. The head tables are usually kept covered with heavy screen to prevent theft.

A considerable saving is made on the save-all, a small sluice catching the drip from the descending buckets and discharging through the hull, and in the nugget catcher—a short, steep series of riffles over which the fines from the extreme end of the screen pass.

In some cases, as on the Yukon, no mercury is used, and the first section of each sluice is covered with coconut matting and expanded metal. The matting is taken up daily, folded, and washed, and the washings are passed over a special set of riffles. The product is cleaned by panning and finally by dry blowing, while the tailing goes back to the main riffle system. The riffles in the lower sections of the sluices are cleaned up at intervals of a week or two.

In California, mercury is more generally used, up to 3000 lb. weekly on the larger dredges and up to 1000 on the smaller. The loss of mercury in a 6-month campaign may range between 1 and 5 per cent of the total used. When cleaning up at intervals of a week or two, the riffles are lifted out, section by section, and washed off with a hose, and the dirt concentrated by temporary stops placed in the sluices. The concentrate thus obtained is shoveled out and washed in a small sluice box, the product screened, and the fines run through an amalgam barrel with a little additional mercury.

Sometimes a trough is inserted below a stop to divert the material being washed down into a clean-up box, about 2 × 3 × 1 ft. deep, having several centerboard mercury riffles, the tailing from which passes through a sluice with expanded metal riffles and back to the main dredge sluices.

In many localities, considerable quantities of lead shot, nails, and miscellaneous metallic scrap may be separated in screening the product, and this material may retain more or less amalgam and necessitate working over.

The "black sand" obtained as a by-product in cleaning up placer sluices often contains platinum metals in small proportions, as well as some gold; much of the gold

and platinum may be recovered by treatment with a suitable concentrator. The Senn machine has been found well adapted for this purpose.

Dry Concentration.—A clean-up of placer material is often finished dry. After removing the coarsest portion with a sieve, the remainder is "tossed" or jigged dry in a pan or shovel, using a circular motion; the sand thus brought to the surface is then blown off. The tailing thus obtained often contains fine or flaky gold.

Dry washers or concentrators are used under desert conditions. The success of all these devices depends on the material being perfectly disintegrated and thoroughly dry; clay, especially, must be pulverized. Several different principles have been applied:

1. Winnowing, by letting material fall vertically through a horizontal blast of air, which is either constant or rapidly pulsating. The wind is often utilized, and the gold caught on a sheet of canvas, but some efficient machines, as that of Edison, have been devised on this principle.

2. Passing the material over an inclined table covered with cloth, supported by wire screen through which a pulsating blast of air rises; the table may be fixed or oscillating, and is provided with low riffles.

3. Passing material over a reciprocating table of the Wilfley type, having a tight cover near the surface, a blast or numerous parallel blasts of air passing parallel to the surface under the cover.

4. Sized material is allowed to fall on a horizontal rapidly rotating disk (as in the Pape-Henneberg system), the particles being thrown to distances varying with their specific gravity.

Black Sand.—The treatment of the black sand or concentrate obtained from beach or alluvial deposits is usually crude and unsatisfactory. This material actually varies much in color; it often consists largely of magnetite and ilmenite, with other heavy minerals such as garnet, tinstone, columbite, or tantalite, and occasionally metals of the platinum group. The gold is retained by, but rarely contained in, the sand particles. The black sand separated by "blowing" at the final stages of a clean-up may show gold values up to \$1 per pound.

Magnetic concentration is rarely of use, as much of the fine precious metal may be picked up mechanically with the magnetic concentrate, while in some cases some of the valuable materials are strongly magnetic. In some river gravels, and such beach sands as the Nome deposit, preliminary separation by 30- or 40-mesh, or finer, screens allows all the gold to pass and retains only pebbles of extremely low grade.

There is no apparent reason why black sand thus concentrated, or recovered from sluices, etc., should not be successfully treated by cyanide solution, after removing coarse gold by riffles or amalgamation. Early experiments are said to have failed in precipitation by zinc, but laboratory tests show no cause for difficulty.

Blanket Concentration.—Woolen blankets have long been used for catching gold at Brazilian mines, where mercury is sickened by bismuth and tellurium minerals, and they were introduced into early Californian and Australian mills and have been used in mills treating the richer Cripple Creek ore. They are generally laid overlapping on inclined tables, the pulp flowing over them for an hour or several hours, when they are folded, replaced by fresh blankets, and the accumulation washed off in a tank.

In 1918, corduroy was used to replace copper plates in the Van Ryn (Rand) stamp mill after adoption of coarse crushing (but not in the tube-mill section); the concentrate (0.27 lb. per ton milled, containing 2.1 per cent gold) was ground in a barrel with mercury, then passing to a mechanical batea. The loss of mercury in the barrel was only 0.01 oz. per ton milled.

In 1923, F. Wartenweiler announced the total elimination of plate amalgamation in two Rand mills, Modderfontein East using five overlapping rows of corduroy strips, which caught, respectively, 80, 11, 4, 3, and 2 per cent of the total catch. The area of corduroy was 1.26 sq. ft. per ton milled daily, and this might have been reduced nearly 50 per cent without serious detriment. The product (1.8 lb. per ton milled) was saved by hand washing, but washing machines might be used; it was treated on a Wilfley, and this concentrate amalgamated in a barrel, yielding 94 per cent of its gold content, 98 per cent of which was free. Corduroy and wool blankets were found equally effective, but corduroy gives a less bulky concentrate, and the lock-up of gold is very small. Canvas gave a still smaller bulk, but caught only 75 per cent as much gold; riffles were only 57 per cent as effective.¹

Canvas concentration, as practiced in California, is particularly adapted to catching extremely fine free gold, galena, and telluride which occur in unsized pulp, and was originally suggested by Brazilian practice. It has been successful in treating tailing that has passed vanners, etc., and still carries 50 cents to \$1 per ton.²

Heavy canvas is laid on a carefully built wooden floor, usually in strips about 22 in. wide, occasionally up to 6 ft., with strips of pine about 1 × 3 in. between for walking on. They are usually 12 to 16 ft. long and inclined 1 to 1.5 in. per ft., but have been made much longer and inclined ½ or ¾ in. Dressed 1-in. lumber is used, free from knots, preferably tongue and grooved, laid on inclined joists, and most carefully leveled. Two launders supply pulp and clear water at the head; one across the foot carries off tailing, and another beyond it the concentrate. After the pulp has run about an hour, the feed hole is plugged on two sluices and the clear water turned on, washing the light sand from the canvas into the tailing launder. As soon as the concentrate in the first sluice is clean, a board or iron sheet is turned or slipped under the lower end of the canvas to convey the stream to the concentrate launder, and the concentrate is sluiced down by a small additional stream from a hose with flat nozzle, or is slightly swept down with a broom. Two sluices are thus idle during cleaning, one sluicing and the next washing. The concentrate passes to a series of settling tanks, the last being provided with baffles. The product is fine, with little sulphide, often over 90 per cent gangue, usually \$30 to \$100 gold per ton, but sometimes much richer. The use of burlap in the tailings launders of Utah Copper to catch some gold minerals has already been commented on—30,000 sq. ft. is used for 24,000 tons of tailing per day, and the burlap is burned monthly.

Important points are perfect adjustment of slope on substantial foundations, equal distribution of pulp and avoidance of overload and dry spots, ample water supply, ample time and space for settling concentrate. Old canvas needs less water than new, producing less but richer concentrate; it may be turned when one side is worn smooth, and is at its best when the original fuzz has just disappeared. If a plant is shut down, it is advisable to keep the canvas wet or remove it and roll it up.

AMALGAMATION

Amalgamation.—Pure gold foil, annealed by gentle heating, is instantly amalgamated if brought into contact with clean mercury at room temperature. It hammered repeatedly, or if previously heated to the point of fusion, it is less easily amalgamated; silver and silver-gold alloys are also less amalgamable; and it is necessary to rub or scour copper with sand, or to treat it with acid or a cyanide solution,

¹ The use of blankets, cloth, and riffles for gold and other minerals is described in Agricola's Book VIII; see especially pp 309, 317, 328, and 331 of Hoover's translation Practice at Grass Valley, Calif., is described by J. A. Phillips, "Mining and Metallurgy of Gold and Silver."

² See STORMS, *Eng. Mining Jour.* Vol. 60, p. 29, 441, 466, July 13, Nov. 9 and 16, 1895; PRESTON, California Gold Mill Practices, Bull. 6, California State Mineralogist.

to ensure amalgamation of the surface. Even when amalgamated, the mercury does not penetrate copper appreciably; gold is much more readily penetrated, and silver slowly. Gold and silver, if covered with a film of grease, oxide of iron, or tellurium, or of a sulphide, no matter how thin, refuse to amalgamate until the film is abraded mechanically or removed by a suitable solvent. *Also Thaucolite*

Similarly, coatings of oil or oxide on mercury, and especially the conditions known as "flouring" and "sickening," effectually prevent amalgamation of gold. This result may often be obviated by the addition of a little sodium amalgam, or by electrolysis (making the mercury the cathode), but too large a proportion of sodium may result in amalgamating iron and any other base metals in contact with the mercury.

Flouring may be brought about by agitating mercury with water or ore pulp and a trace of oil, or by distilling it from a retort containing a little grease or paper; in extreme cases it forms a mass of microscopic globules, like flour or white grease, which refuse to coalesce. Sickening is a similar, often indistinguishable, condition, induced by chemical means, as when the globules are coated with a film of oxide, sulphide, or chloride of the mercury itself or of some base metal contained in it. It may be caused by agitating mercury with finely divided, partly oxidized sulphides, or by perchlorides of iron, mercury, copper, or other persalts of these metals plus NaCl. Any appreciable impurity in mercury is usually recognizable by the globules losing the spheroidal form and acquiring a tail.

The extraction of gold from ore by amalgamation was practiced to some extent in ancient times, but no details of the methods are known. In the Middle Ages, rich ore and concentrate were ground or rubbed with mercury in wooden bowls using iron-shod mullers rotated by crude machinery. Later, batches of ore were ground fine with mercury in the arrastra, using stone drags on a stone-paved bottom. In recent times the amalgamation of gold has been almost entirely associated with the development of the stamp mill.

Three variants may be noted: inside amalgamation proper, in which a copper plate is inserted in the front of the stamp mortar, and sometimes a second inside plate at the back, mercury being fed with the ore at intervals varying from 15 min. to 2 hr.; outside amalgamation, in which all the reliance is placed on amalgamated copper plates outside the mortar, on which mercury is sprinkled from time to time; and an intermediate system, in which the mercury is fed into the mortar but no inside plates are used.

Disregarding the crude nonrotating stamps of earlier periods, gold milling since 1850 has included the following:

1. The light (500- to 750-lb.) stamps of early Californian and Australian practice, used three to six in a battery. The mortars were of various patterns, often low iron troughs with built-up housings of wood or sheet iron. The screen was often punched sheet iron or copper.

2. Wide mortars, supposed advantageous for amalgamation, used with stamps of 700 to 850 lb., and of high form. These rarely crushed 2 tons per stamp day, often only 1.25 to 1.5 tons through a 40-mesh or finer wire screen, usually brass wire, or punched tin plate. A drop of 6 or 7 in., ninety to one hundred times per minute, was common.

3. The extremely wide mortar characteristic of Gilpin County, Colorado, with light (600- to 700-lb.) stamps of high drop (about 18 in.) and only 30 per minute, was supposed to have special virtue as an amalgamator.

4. The extremely narrow, high-form mortar, usually associated with Homestake practice (1876) and designed for rapid crushing. An 850-lb. stamp at 88 drops of 10 in. crushed over 4 tons daily through a diagonal iron or steel slot screen equivalent to 30 mesh. Its crushing efficiency has led to the wide use of this pattern and vari-

ations of it adapted for heavier stamps. The narrow form is not necessarily inimical to amalgamation, as it has not been uncommon to find over 50 per cent of the total recovery in the mortar, collected almost entirely on the narrow (5 or 6 in.) chuck-block plate.

5. The more recent heavy stamps, in American and especially in African practice, which have ranged from 1200- to 2000-lb. weight, about 1500 lb. being perhaps more generally preferred. These have tended constantly toward coarser crushing, with screens approaching $\frac{3}{4}$ in. in aperture, the product of over 10 tons per stamp passing to rod mills, ball mills, or pebble mills. With the heavy castings, long heads, etc., necessary for heavy weight, the open-front mortar has been revived; and the coarseness of crushing has encouraged the abandonment of inside amalgamation.

Five stamps per battery was early recognized as standard practice, mortars discharging in front only, and fed with Challenge feeders. Two-stamp mortars have been little used except for prospecting, but excellent results may be obtained with them and with some of the one-stamp mills, of which the Nissen is probably the best. This has been made of 2000-lb. falling weight, with a circular mortar half surrounded by screen. Some others have screen on three of the four sides.

Steel-wire screen is now much used, with either square or rectangular openings, often slotlike, with double wires in one direction and heavily crimped. In fine crushing, sheet steel is often used, punched with diagonal slots $\frac{1}{2}$ in. long, or thin tinned iron plate with round punched holes. The modern screens are almost always set vertical.

In place of a long line-shaft drive, one electric motor now usually drives 10 light or 5 heavy stamps, by a built-up wood pulley 7 or 8 ft. in diameter with a 14- to 18-in. belt, the shaft running in plain cast-iron bearings without cover. Wrought-iron camshafts are preferable to any steel ordinarily obtainable. The cams are preferably attached by the Blanton self-locking device, which allows of easy removal, all the cams being interchangeable in position.

The standard cam curve is the involute of a circle, the center coincident with the camshaft axis and the radius the distance from the axis to the central plane of the stamp stems. The involute gives uniform speed of lift, but strikes the tappet with a sudden jar, and the curve is often much modified at root and tip. The gib tappet may have two or three keys. The usual order of drop is 1, 3, 5, 2, 4 (identical with 1, 4, 2, 5, 3), the only combination possible if no adjacent stamps drop consecutively, but 1, 5, 2, 4, 3 (= 1, 4, 2, 3, 5) is also used, and occasionally others in which one adjacent pair drop consecutively. Any tendency to bank sand at one end of mortar is usually overcome by giving the end stamp a slight increase in drop. Various forms of guide are used but generally have cast-iron liners in place of the wood formerly used.

For stamps from 800- to 1500-lb. weight the following table gives the range of weights commonly adopted. The last column shows the greater range of weight used for heavy stamps in South Africa and India. The percentages are based on falling weight with new shoes.

	800 to 1,500 lb., per cent	1,250 to 2,000 lb., per cent
Stem.....	42-44	47-28
Tappet.....	16-13	10-14
Boss.....	26-28	22-40
Shoe.....	17-14	20-13

The corresponding cam weight ranges from 25 per cent with light, to 20 per cent with heavy stamps, all being about 32 in. across tips. The camshaft ranges from (for 10) 30 per cent above the falling weight for light up to 50 per cent above for heavy stamps ($5\frac{3}{8}$ to $6\frac{1}{2}$ in. by 14 to 16 ft.); stems increasing from 3 in. at 800 lb. to 4 in. at 900, and usually 14 ft. long; shoe diameters 8.5 in. up to about 900 lb., and 9 in. above that.

Mortars are always of the high form, of heavy cast iron, generally with front entirely open, but variously proportioned. Reinforced concrete is now in general use for mortar supports, with an intermediate cushion of wood and rubber or belting. The ends and back of mortars are often protected by liners of chrome or manganese steel.

Battery water should be supplied at the rear of the mortar at two or more inlets; the ratio of water to ore stamped has varied widely, ranging from 2.5 in occasional Californian mills to 10 or 12 in former Homestake practice, high crushing duty and amalgamation being obtainable at both extremes—5 to 8 is generally preferable. With plate amalgamation, the water and grade must be sufficient, and the distribution of pulp over the topmost plate even enough to produce uniform waves and avoid building up islands of sand. For successful amalgamation the temperature of the feed water should be uniform, and neither extremely cold nor hot. Practically all the energy expended in crushing reappears in the increased temperature of the pulp, which is of importance in cold climates.

Amalgamation.—Mortars formerly had inside plates both front and back 6 or 8 in. wide and extending across the full length; the back plate has been discarded and the front plate—usually about 5 or 6 in. by 14 in. thick—is attached to the chuck block immediately beneath the screen; even this is now obsolescent and is seldom used with heavy stamps.

A "lip plate" is sometimes attached outside the mortar, extending across the discharge and 1 to 2 ft. wide. The main apron plate may be in one unit or more, each 4 to 5 ft. wide by 8 to 12 ft., of 18-in. soft-rolled copper. In successive units, the width should be maintained or increased. Long plates are usually set in an unbroken sheet of 8 to 24 ft., but some operators claim an advantage in cutting them into 2-ft. lengths, set with a drop of an inch or two at each step; the long plates are easier to clean and care for. Plates of Muntz metal have been used in New Zealand and elsewhere with apparent success; at several mills in the United States they have been a total failure. The plate table is best built of tongue-and-grooved lumber, 1.5 or 2 in. thick, with 2-in. sides, and may be made adjustable in slope. Planed cast iron has been used. The plates are secured by screws or copper nails, and cleats are often added at the sides. If divided longitudinally into two or three runs, it is easy to clean one run at a time without stopping the battery.

The inclination of plates is best kept from 1.5 to 2.5 in. per ft. (12.5 to 20 per cent) depending on the proportion of water, fineness of pulp, and proportion of heavy minerals, but extremes of $\frac{5}{8}$ in. up to 3 in. per ft. have been used. The plates are usually placed close to the mortar, but sometimes the pulp is transported some distance and then redistributed over a plate system. This sometimes results in large accumulations of amalgam in pipes or launders.

Silver plating of the copper plates is advantageous, except with rich ore, and in the case of the plate next the mortar; about 2 oz. silver per square foot is a suitable amount, or soft silver amalgam may be rubbed on the plate. In "setting" new copper plates, about $\frac{1}{4}$ oz. mercury per square foot is requisite, and this should be applied by scouring with wet sand and a little weak solution of sodium cyanide.

Various amalgam or quicksilver traps have been used, but there is probably nothing better than a shallow transverse trough or riffle about 2 in. deep and 4 or 5 in. wide

at the foot of the plate table. The accumulated concentrate from this may be collected daily with a small scoop and carried in buckets to a central point, where it can be run over a special plate or riffles, or ground in a pan or small ball mill.

Many mechanical amalgamators have been devised and used, such as horizontal rotating cylinders lined with copper, or provided with copper wings or lifters, or arrangements of horizontal disks or shelves rotating on a vertical axis, series of shelves of sheet copper, etc. The Pierce amalgamator is probably the only one of these to show greater efficiency than a plain plate. Numerous electrolytic devices have also been used, as well as sodium and zinc amalgam, to maintain the surface of mercury in a bright condition.

It is remarkable that gold or amalgam, while escaping all the contrivances arranged to catch it, often accumulates in unexpected places, such as angles of cones, sumps, and launders, the rakes of Dorr classifiers, and on the runners of high-speed centrifugal pumps. All such places should be inspected from time to time, and any tendency to build in launders should be encouraged by placing riffles suitably safeguarded.

Plate Area.—The relation of plate surface to stamps and stamp capacity varies remarkably in the practice of different fields. Some extreme cases may be noted:

Mine or district	Approximate percentage of product amalgamated	Square feet plate area	
		Per stamp	Per ton per day
Treadwell, Alaska—880 stamps, 1904.....	50	9	2
Homestake, Amicus mill, 240 1910.....	70	62.1	13.6
S. D. stamps 1923 with tubes.....	66	43.3	7.8
Pocahontas mill, 1910.....	70	32.7	7.5
160 stamps 1923.....	66	18.0	3.6
South mill, 120 1923 with rod } mills }	66	25.6	1.6
Rand, South Africa—Typical mill with tube mills	65	10	1.2
Ooregum, India—55 stamps, 1923 with tubes...	88	20	2.2

With the revival of blanket practice the tendency is to reduce plate area still further.

Loss of Mercury.—In gold amalgamation, an ounce per ton was not an uncommon loss in early practice, and occasionally much higher losses were recorded, but this has been much reduced. At the Treadwell mines, shortly before abandoning amalgamation, the loss varied from 0.06 to 0.08 oz. per ton with ore from \$1.50 to \$2.50; at the Homestake, 0.06 oz. was lost with low-grade oxidized ore, and 0.17 oz. with \$5-ore containing sulphides, and a similar range has prevailed in South Africa. At Modderfontein East, amalgamating corduroy concentrate, about 0.05 oz. is reported.

Among the principal sources of loss are drops running from the end of plates kept too "wet," and flouing.

Outside plates usually have the amalgam removed once every 24 or 48 hr. by washing off sand and then brushing thoroughly after sprinkling with some additional mercury. The amalgam may then be collected at one spot by means of a stiff brush or cloth, or a rubber scraper, and transferred to an iron kettle. Any hard crystalline accumulations should be carefully scraped off before they become persistent. With a

Fe is acting as a catalyst

properly organized system the entire time consumed is about 1 min. per stamp per day. In many mills the plates are also "dressed" or brushed up at intermediate periods, and may be sprinkled with mercury at the same time. Inside plates are usually removed for cleaning about twice a month, a clean plate being exchanged for the one taken out. The entire mortar is cleaned out about once a month, or whenever dies are taken out.

The actual absorption of precious metal into the body of a copper plate is negligible, but the accumulation on the surface may amount to many dollars per square foot if accretions of hard amalgam are allowed to build up, as they sometimes do, to a thickness of $\frac{1}{4}$ in. or more, thus tying up an important amount of gold. In some mills this layer is softened by the occasional application of steam or hot sand, which facilitates its removal by scraping, but it is better to avoid this condition by daily removing hard accretions. Absorption only occurs when the rolled copper plate has capillary openings, such as minute cracks or pinholes.

Amalgam obtained from plates, etc., is cleaned by grinding with water and additional quicksilver, the floating impurities being wiped from the surface with a sponge, or in small lots by pouring from one vessel to another, when pyrite, etc., adheres to the moist vessels. Metallic iron is removed by a magnet. Small lots are ground by hand with a pestle and mortar of iron or wedgwood ware; on a larger scale the amalgam, or accumulated cleaning, is treated in a miniature iron tube mill, or a Knox or Berdan pan. The tube mill may be 2 ft. in diameter by 1 to 4 ft. long, with steel balls or rods of drill steel; it may be worked in batches through a covered hand hole, or continuously by a stream of water passing through hollow trunnions. The Knox pan is a small cast-iron pan with a muller carried on a vertical shaft; the Berdan revolves on an inclined shaft, grinding by means of two or three large balls, or by drags chained to a fixed post.

The amalgam is squeezed in fairly heavy (10-oz.) canvas; the finish is usually given by hand in balls of about 100 oz. each, or in cylinders compressed in a hydraulic machine with disks of canvas and coconut matting at each end; the removal of excess mercury is facilitated by heating the balls in hot water.

A high "percentage of retort" is favored by a large percentage of gold in the resulting bullion, coarseness of the original particles of native gold, frequency of clean-ups (giving mercury less time to penetrate), pressure applied in squeezing (much increased by use of machine), and high temperature during the squeezing. About 60 per cent is occasionally reached, while silvery amalgam may yield only 25 per cent; 35 per cent is about average for hand-squeezed amalgam.

Amalgam retorts are made in the pot form for charges up to about 2000 oz., and should be not over two-thirds filled. For larger amounts the cylindrical built-in form should be used, fitted with three or four light cast-iron trays. The trays or pot retorts are given an internal wash of wood ashes, fine clay, or chalk, or are painted with iron oxide, to prevent adhesion of bullion. Paper is sometimes used, but may cause flouing of the mercury. The covers or doors are best sealed with a lute made of sifted wood ashes and secured by well-driven wedge keys. A long condenser should be used, with a jacket supplied with cold water. In large retorts it is convenient to use loose dividing pieces of sheet iron, similarly painted, so that the resulting bullion will readily fall into pieces of convenient size for charging into crucibles.

Any convenient fuel may be used in retorting, and a pot retort may be heated in any style of melting furnace, or in the open if surrounded by a piece of sheet iron, but it is essential that the top be covered and kept hot, or the mercury vapor will condense before escaping. The temperature of boiling mercury is 356°C. (672°F.) and its latent heat 125 B.t.u. per lb. On account of the high specific gravity of the vapor (seven times that of air), the discharge pipes should point downward as far

Also Free Amalgam Prior to Retort

Wrong
when
Au is in
colloidal
state or
ionic

as possible and means should be adopted to carry off any escaping fume and prevent its inhalation, especially if it is necessary to open the retort before it has time to cool. The mercury carries over a trifling amount of gold, most of which is due to spattering in the earlier stages of volatilization. The loss of mercury should be very small; any considerable difference in the weight of amalgam and of bullion plus mercury points to a defective lute or a leaky retort.

Bars of mill bullion or refined cyanide product are melted in graphite crucibles with borax sufficient to form a cover, and poured into iron molds previously smoked heavily or coated with graphite. About 2000 oz. is the usual weight limit for gold bars, and about 1000 to 1200 oz. for silver.

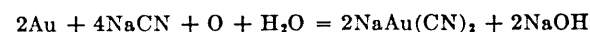
Bars containing gold and silver with little base metal other than copper suffer very little segregation and solidify rapidly. In sampling them it is safe to chip from one corner at the top and the opposite corner at the bottom or to drill $\frac{1}{4}$ - or $\frac{3}{8}$ -in. holes at opposite corners. Cyanide bars containing lead or zinc are irregular in composition and should be sampled from the crucible just after stirring, or a sample may be taken while pouring by deflecting some of the flowing metal into a vessel of water.¹

As soon as the bullion solidifies in the mold, the slag may be removed by pouring water on it and scraping it out, or by plunging the hot bar into cold water. Plunged bars retain a little water if the surface is rough.

CYANIDATION

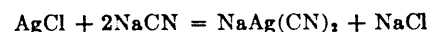
Cyanidation.—At the present time sodium cyanide, NaCN, has entirely superseded potassium cyanide, KCN, as a solvent, and it alone will be considered here, although some metallurgists still make all calculations in KCN and recalculate the results to the actual salt used.²

The essential reactions of the cyanide process are, for gold,



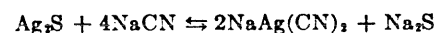
This is Elsner's reaction, verified by Maclaurin, indicating the necessity for oxygen or its equivalent. Metallic silver follows the same reaction, substituting Ag for Au. Cyanides of other alkali and alkali-earth metals act in precisely the same way, substituting Ca, Ba, 2K, etc., for 2Na. Hydrocyanic acid is an extremely feeble solvent, and cyanogen itself is without action on gold.

Silver chloride is rapidly dissolved, without oxygen,

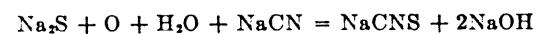


and most other silver compounds are similarly dissolved.

Silver sulphide, however, dissolves slowly, the reaction being reversible and requiring an excess of cyanide.



Artificial gold sulphide is similarly dissolved. The solutions obtained always contain more or less thiocyanate (NaCNS), and this probably results from oxidation of the Na_2S .



Free sulphur, resulting from partial oxidation of pyritic ore, or sulphur from thiosul-

¹ See Sampling, pp. 72, 76, 78, and 80 of the volume entitled "Principles and Processes."

² It is convenient to remember that, for all practical purposes, 4 lb. KCN = 3 lb. NaCN, and 1 lb. of 98 per cent NaCN = 2 lb. of Aero containing cyanogen equivalent to 49 per cent NaCN. Also that 10 cc of 0.5N AgNO_3 (8.50 g. per l.) = 0.049 g. NaCN = 0.05 g. of 98 per cent salt, or 0.1 g. of Aero at 49 per cent.

phates formed by the action of lime or soda on pyritic ore, also reacts on cyanide with formation of thiocyanate.



Tellurides of gold and silver are scarcely affected by cyanide solutions, and silver selenide is very slowly attacked.

ELECTROMOTIVE FORCE OF METALS IN CYANIDE SOLUTIONS¹

Concentration KCN	Most probable value for e.m.f.						
	Zinc	Cop- per	Gold	Silver	Lead	Mer- cury	Iron
6.5 per cent = N	+0.945	+0.930	+0.42	+0.34	+0.20	+0.15	-0.03
0.65 per cent = $N/10$	+0.870	+0.68	+0.265	+0.195	+0.16	+0.05	-0.09
0.065 per cent = $N/100$	+0.775	+0.43	+0.09	+0.055	+0.11	+0.04	-0.12
0.0065 per cent = $N/1,000$..	+0.415	-0.05	-0.34	-0.31	+0.07	-0.19	-0.13
0.00065 per cent = $N/10,000$	+0.385	-0.25	-0.45	-0.42	+0.05	-0.59	-0.14

¹ CHRISTY, *Trans. A.I.M.E.*, Vol. 30, pp. 921-922.

As calculated from the chemical equivalents, 1 lb. NaCN suffices to dissolve 1.1 lb. Ag or 2 lb. Au; 1 lb. Zn to precipitate 3.3 lb. Ag or 6 lb. Au. An ounce of metallic silver, therefore, requires 1.8 times as much of either reagent as an ounce of gold, and a dollar's worth of silver at the ordinary range of price uses forty to sixty times as much as a dollar's worth of gold. In practice, the difference is even greater because, as a rule, gold dissolves readily in dilute solution, while silver often occurs as the sulphide, which requires a stronger cyanide solution owing to the reversible character of its reaction. On the other hand, silver chloride dissolves rapidly and with little decomposition of cyanide.

Under identical conditions, metallic silver dissolves about half as fast as gold, or in exact proportion to their atomic weights. Silver-free gold dissolves more readily than gold alloyed with silver. Maclaurin showed that all gold-silver alloys should dissolve in cyanide solution at the same rate as measured in thickness removed, and in the same proportions in which they exist in the original alloy; Yokobori and others confirm this.

As regards the effect of amalgamation on the rate of dissolution by cyanide, some contrary evidence has been adduced. In stationary beaker tests with pure gold foil, a mere film of amalgam retards solution about as much as thorough wetting with mercury—similar pieces show one-half to one-tenth the rate of solution noted with clean gold; when agitated in sand mixtures the same tendency is noted.

For a given percentage of NaCN, gold in a thick slime mixture dissolves much less rapidly than in thin pulp, the same is true of silver, of oxygen, and of salts such as NaCN itself—lumps of which should not be dumped in agitators but predissolved in clear solution or water. This effect seems to be partly due to the greater viscosity of thick pulp, partly to the smaller proportion of solution to unit volume and unit surface.

After a certain period of contact with a given solution, the dissolution of gold from ore practically ceases, in spite of agitation and ample aeration; on adding fresh solution, or replacing a part with barren solution or even with water, further dissolution takes place. This is more marked with silver than gold, and especially on adding

aerated barren solution from extractors. Some of the effect is, no doubt, due to the inert or "fatigued" solution having reached an equilibrium with the ore, but probably much of the later apparent dissolving is actually diffusion of the richer solution adsorbed or absorbed by the ore particles.

In sulphide ores, especially complex sulphosalts, silver may be very slowly soluble; this may often be partly overcome by removal from the solution of the Na_2S formed by means of lead compounds; mercury salts are sometimes used with advantage, and fine grinding is essential. Owing to the reversible character of the reaction with Ag_2S , a short treatment with very strong (1 per cent or more) solution of NaCN is often much more effective than long treatment with dilute.

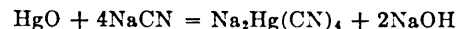
The best strength of solution must be determined by experiment. In agitation systems, coarse gold being removed if originally present, slime may be treated with solution of 0.1 to 0.01 per cent NaCN ; silver slime may require 0.2 to 0.5 per cent or higher.

In well-roasted sulphide ore or concentrate the gold is, as a rule, amenable to cyanide, but the globular particles from roasted tellurides dissolve slowly; silver in similar roasted material becomes partly insoluble; extremely fine grinding is desirable with most rich silver material. After fine grinding, such material is sometimes put back in the same circuit with average ore; it is best first to give it a separate intensive treatment with strong solution.

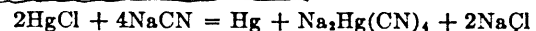
Gold telluride ores must be either roasted or treated with some oxidizing agent, such as bromocyanide, BrCN , after preliminary leaching; or any alkaline bromate, or peroxide of sodium or barium, may be used after preliminary treatment with NaCN .

Many other oxidizing agents have been tried in connection with cyanide treatment, to supply "nascent CN" or its equivalent, but none has been able to compete with atmospheric oxygen for ordinary ores.

Lead and Mercury in Cyaniding.—Mercuric oxide and chloride dissolve completely in cyanide solutions



but when mercurous oxide or chloride is treated with alkaline cyanide, half the mercury remains insoluble in the metallic state.



An old tailing pile containing HgCl , therefore, cannot be expected to yield 50 per cent of the mercury by cyaniding; mercuric oxide would give an almost complete recovery; the sulphide and metallic mercury would yield little or nothing.

Lead is sometimes added to solutions as the acetate (54.6 per cent Pb) or nitrate (62.56 per cent Pb), the latter being generally more economical. Litharge ($\text{PbO} = 92.8$ per cent Pb) is sometimes added to grinders, or ground with lime. In alkaline solutions the lead is dissolved as plumbite, Na_2PbO_2 , which reacts with sulphides to form PbS . Occasionally, a local oxidized lead ore (PbCO_3) has been similarly used. Removing Na_2S , lead facilitates the solution of Ag_2S , argentite, but it has no beneficial effect on the complex sulphosalts of silver. Mercury would similarly precipitate the sulphide radical as HgS . Both lead and mercury also influence precipitation. Contact with zinc dust or shaving at once throws down metallic lead or mercury, forming a zinc-lead or zinc-mercury couple which facilitates precipitation of gold and silver, and is especially advantageous when zinc shaving is coated with copper. Lead added to solutions at the time of precipitation is found in the precipitate, and is sometimes troublesome in refining unless cupellation is practiced. Any mercury in solution is similarly precipitated, and when zinc precipitate contains much (say 10 per cent) of it, its removal by distillation may be profitable.

Losses of Cyanide.—Losses of cyanide are mechanical and chemical. The first comprise the cyanide that is carried off in solution, some of which may be unavoidably thrown away daily, to prevent accumulation of too great a volume, or may be discharged in the residue, the washing of which is necessarily imperfect.

Chemical losses include that due to hydrolysis of NaCN ($2\text{NaCN} + \text{H}_2\text{O} = 2\text{NaOH} + 2\text{HCN}$), but this effect is slight in solutions that are distinctly alkaline, and is much smaller in old solutions [which often carry most of their CN in the form of $\text{Na}_2\text{Zn}(\text{CN})_4$] than in simple NaCN ; decomposition of NaCN by acids, including CO_2 contained in air used in agitation ($2\text{NaCN} + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{HCN}$); oxidation of NaCN by oxygen of air to form NaCNO and other inactive compounds, such as bicarbonates ($\text{NaCN} + \text{O} = \text{NaCNO}$; $2\text{NaCNO} + 3\text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{NH}_3$, etc.); reaction with iron compounds, copper, etc., to form Prussian blue and various double cyanides, and with sulphur to form NaCNS .

Cyanicides.—"Cyanicide" is a convenient name applied to all those substances found in ores and tailings which cause a loss of the essential ion CN from the solutions used in treatment. Under this head may be grouped acids that directly decompose NaCN (including carbonic and humic acids); salts such as sulphates and arsenates, especially those of iron, which consume free alkali [$\text{Ca}(\text{OH})_2$ and NaOH], thus facilitating the hydrolysis of NaCN ; ferrous salts and oxidized compounds of copper and zinc which form complex cyanides, either entirely inert or feeble solvents for gold and silver; and certain sulphur compounds that react with NaCN to form NaCNS .

When used injudiciously and in excess, even oxygen, chlorine, bromocyanide, peroxides, and other oxidizing agents are actually cyanicides. The cyanide actually used in dissolving gold is almost negligible, but rich silver ore consumes more—100 oz. of silver using over 6 lb. NaCN to form the double cyanide.

Copper in oxidized ores is usually in the form of the green or blue carbonate (malachite or azurite), an oxide, basic sulphate, or occasionally the metal. In pan-amalgamation tailings it occurs in similar forms from decomposition of added sulphate. In all these forms it is readily dissolved by cyanide solutions and decomposes or renders useless approximately three times its weight of NaCN , or four times of KCN . In the case of KCN , the actual cuprous compound formed appears to lie between $\text{K}_2\text{Cu}'(\text{CN})_2$ and $\text{K}_2\text{Cu}'(\text{CN})_4$, while a portion of the CN is oxidized to CNO in reducing combined Cu'' to Cu' . As little as 0.1 per cent of soluble copper may, therefore, cause a loss of several pounds of cyanide per ton treated. Unoxidized sulphide ores are commonly but little attacked and decompose relatively little cyanide.

From some oxidized ores it is possible to remove the soluble copper by dilute ammonia, or, if but little calcium carbonate is present, by dilute sulphuric acid; in either case the dissolved copper must be removed by thorough washing before contact with cyanide solution. Cu
Remov

Iron and steel in the form of sheet metal, etc., are practically without effect on cyanide solutions. Some writers have insisted that the fine metallic iron introduced into ore by wear of mill castings, steel balls, and rods, etc., which may range from 1 to 5 lb. per ton, decomposes cyanide and interferes with gold extraction. In practical tests, it is difficult to recognize any losses due to metallic iron as such. Any actual decomposition is probably due to ferrous compounds produced by oxidation of this finely divided metal, or by the action on it of acids resulting from oxidation of sulphur compounds in the ore. ✓

Antimonial Ores.—Ores containing antimony as sulphide (stibnite) have, in some instances, given trouble in extraction, and also by yielding an impure precipitate, difficult to refine unless cupellation is practiced.

Fine grinding has been recommended, and the use of a solution as low as possible in cyanide and especially low in free alkali. In other cases some success has been

reported in the adoption of a treatment with comparatively strong solution of sodium hydroxide or sulphide to dissolve interfering antimony compounds, and washing out the solution before cyaniding.

In some antimonial ores, as with others containing Se or Te, all or most of the gold may resist both amalgamation and cyanide, and may also be impossible to concentrate. A thorough roast, followed by fine grinding, generally renders a high percentage soluble in cyanide solution.

Arsenical Ores.—Many of the common arsenical minerals, notably arsenopyrite, FeAsS, are totally unaffected by cyanide solution; their oxidation products are, however, soluble in many cases. When arsenic passes into solution, some of it may appear in the precipitate, and in this case extreme precautions must be taken in disposing of the fumes from acid treatment, which may contain arsine, AsH₃.

The presence of manganese minerals in gold ores appears to have no ill effect in cyaniding; some silver ores contain large percentages of manganese peroxide but yield readily to cyanidation; others, some of them containing relatively small proportions of manganese, yield only a small percentage of their silver, even to strong cyanide solutions. Mere addition of MnO₂ has no prejudicial effect, and it is probable that in the latter ores a more or less definite manganite of silver exists, analogous to the compounds of barium and copper found in psilomelane. Investigations by R. Linton, E. M. Hamilton, and W. H. Coghill show that in some cases treatment with dilute hydrochloric acid, salt and sulphuric acid, sulphur dioxide, hydrogen sulphide, or a sulphhydrate, or a chloridizing roast leaves the silver in a form permitting a high extraction with cyanide solution, though it may be insoluble in nitric acid. Reagents that decolorize the dark manganese compounds generally free the silver.

For instance, Hamilton, in one case, extracted only 5 to 15 per cent at 200 mesh, additions of lead, oxidation, hot solutions, chlorine, and sodium sulphide, Na₂S giving no improvement. A preliminary treatment with H₂S or NaHS increased the extraction to 73 per cent, HCl to 94 per cent, 5 per cent SO₂ to 84 per cent, and a chloridizing roast to 75 per cent, when followed by agitation with dilute KCN solution. Concentration, oil concentration, and flotation gave no results.

The Caron process commences with a "reducing roast" to decompose peroxides, and in certain cases has greatly increased the subsequent extraction of silver.

Calcium sulphate is sometimes an original constituent of ores and tailings and of some waters; more commonly it results from the roasting or weathering of calcareous ores containing sulphides, and occasionally from the action of sulphuric acid on such ore. Lead sulphate may also react with lime solution to give a saturated solution of CaSO₄. In Colorado and Western Australia, leaching of roasted ore has sometimes been followed by the setting of charges to a cementlike mass, which might require blasting. A more common result is the supersaturation of cyanide solutions with CaSO₄, which crystallizes as a hard deposit on pipes, canvas, etc., and may coat zinc shavings so as to render them inactive. A complication is caused by the fact that the solubility of CaSO₄ in water decreases with a rise of temperature.

Magnesium sulphate may be similarly formed; while readily soluble, it is equally objectionable owing to the flocculent precipitate formed when its solution is mixed with another differing in alkalinity.

Owing to the presence of carbonaceous matter (not graphite) in black schists associated with the ores, it has been impossible to secure good extractions of gold at certain mines in various parts of the world, much of the gold being reprecipitated as soon as dissolved in some form which has never been positively identified, though much has been written on the subject. Charcoal from charred mine timbers, etc., similarly interferes.

Mn₂O₃
Freeing Ag from Mn

Note
Carbonaceous
ores

In the case of some African ores, a process was worked out by Feldtmann and Wartenweiler for extracting the reprecipitated gold by a subsequent leaching with sodium sulphide solution.

A more recent method is that of Silver and Dorfman, who give the ore a preliminary agitation with a little flotation oil, which prevents the carbonaceous matter from interfering.

Some pyritic concentrates oxidize rapidly to FeSO₄, etc., and then decompose large amounts of NaCN, forming ferrocyanides, Prussian blue, etc. This may be obviated by a fairly long aeration in the presence of lime or soda, oxidizing the iron completely to ferric hydroxide.

At the Goldfield Consolidated mill the concentrates contained copper as well as iron sulphates. Soluble copper and iron were removed by preliminary treatment with dilute sulphuric acid, followed by an alkaline wash, after which the fine-ground concentrate was cyanided in a Pachuca tank with repeated decantation, finishing in a Kelly filter.

Lime is used in cyaniding to neutralize acid existing in ore, or the "latent acidity" of such salts as basic ferric sulphate, thus protecting cyanide from decomposition. It is also of value in increasing the settling rate of slime.

When crushing in water, quicklime may be fed dry with the ore, or may be slaked or ground in a tube mill or pan. This early introduction effects neutralization at the earliest possible stage, but sometimes has an adverse influence on amalgamation. It is advisable when crushing in cyanide solution. An opposite policy is followed at the Homestake sand plants, where the ore develops acidity by oxidation and a granular lime is required for progressive neutralization; here it is crushed by a stamp through a seven-mesh screen and mixed with the sand just as it passes to the collecting-leaching vats.

In treating dry sand, the lime should be slaked carefully, and the fine product mixed as uniformly as possible with the charge at any convenient stage. With slime pulp, it may be used as milk of lime fed from a grinding pan or mixer. Acid and bicarbonate waters consume an appreciable quantity of lime. In some cases, as when aluminum is used as a precipitant, the calcium in solution must be replaced by sodium, by the use of caustic soda or soda ash.

An excess of alkali in solution protects NaCN from hydrolysis, but it usually retards and may even prevent the dissolving of gold and silver, especially with sulphide ores. Alkalinity must, therefore, be carefully controlled, and it is generally best to maintain it at the lowest possible point in excess of that corresponding to the cyanide (NaCN) indicated by titration—in other words, the protective alkali should be as near to zero as possible. This is generally safe, as old solutions containing zinc show little tendency to hydrolysis of HCN.

Lime should be free from charcoal and contain but little magnesia. The available CaO in good quicklime is between 80 and 90 per cent; it is easily determined by shaking 2 g. with 20 g. of sugar in 200 to 1000 cc. of distilled water, and titrating one-twentieth of the clear liquid with standard acid.

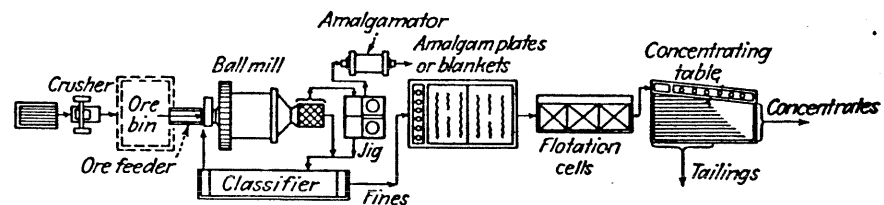
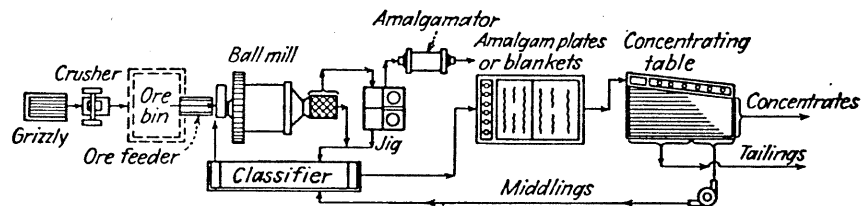
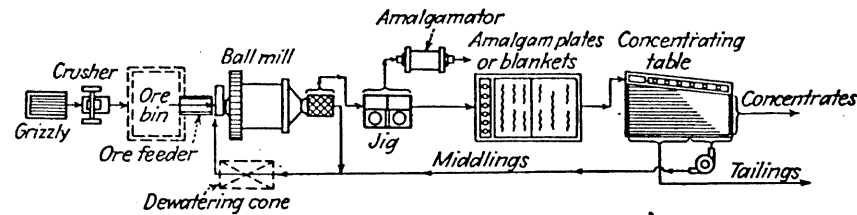
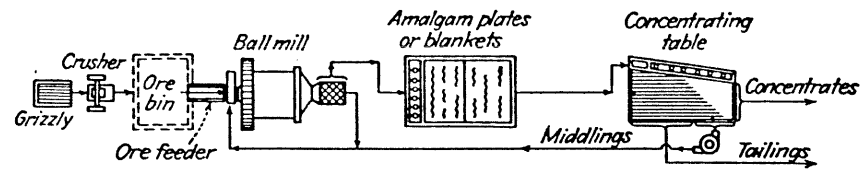
Sand and Slime.—In the first MacArthur-Forrest patents, agitation in cyanide solution is indicated, but in the early practical plants some form of separation was found necessary, the coarser material, including as much of the fines as possible, was leached, the "slime" being allowed to accumulate untreated, unless exceptionally rich.

"Slime" properly refers to colloidal material—"superfine particles"—which can be neither leached nor settled readily; Gross has defined it as "anything which renders water muddy." The slime separated by classification is largely extremely fine sand, the microscope showing this to consist of crystalline particles. Leachable sand

Pachuca

1

Titration



FIGS. 7-10.—Typical flow sheets of successful gold-milling installations:¹ 7, simple flow sheet for high-grade, free-milling ores; 8, an added jig and amalgamation unit give additional recoveries; 9, a classifier in closed circuit increases the grinding and jigging efficiency; 10, flotation cells recover sulphides formerly lost.

¹ These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

may contain 40 or 50 per cent of material finer than 200 mesh, provided true (colloidal) slime is practically eliminated. In general, quartz and pyrite tend to pass into sand during classification, while the slime contains the more basic and hydrous constituents of the ore—especially limonite, and hydrous silicates of alumina and magnesia, such as kaolin and chlorite.

In rare instances, a porous ore, containing no coarse gold, may be crushed coarsely (to, say, $\frac{1}{4}$ in.) and leached directly, but classification is more generally necessary.

“All-sliming” is a term loosely applied to the comminution of an ore to pass 200 mesh—sometimes extended to 100, or even 80 mesh—the general idea being to ensure a product that can easily be kept in suspension.

Crushing in cyanide solution was first attempted by A. B. Paul in California, but was little used until 1899; since then its use has rapidly increased. Milling in water washes out soluble cyanides, and lime may be used to neutralize latent acidity, in some cases saving much cyanide; amalgamation may be thus kept in advance of contact with cyanide. Crushing with cyanide complicates the sampling of heads, owing to dissolved values, but has many advantages, dissolution of gold beginning as soon as the ore enters the mortar or mill, and the only water introduced into the system being original moisture and that used as a final wash. From 50 to 75 per cent of the soluble gold may dissolve during milling, but with silver, solution is much slower.

Sand Leaching.—Sand is leached in vats with filter bottoms, filtration being effected by gravity, in some cases aided by the application of a vacuum beneath the filter. The vats are cylindrical, of steel or wood, redwood or cypress being generally preferred on account of their durability. They must be made absolutely watertight, with substantial foundations, preferably parallel walls of concrete arranged to allow of easy inspection of the bottom and sides. Vats of reinforced concrete have been used, of various shapes, made tight by the use of bituminous coatings. Wooden vats should have the staves doweled, bottom boards either doweled or grooved for the insertion of pine tongues, and bottom end joints made with metal tongues. The bottoms should have a slight slope toward the solution outlet.

Filter Bottoms.—A ring of wood is placed around each bottom, about 1.5 in. from the staves or side, forming an annular channel for the rope used to secure the stretched filter; the height of this varies, but should be 3 to 5 in. for large vats. The space inside this ring is occupied by some form of wooden grid of equal depth. One of the best forms is a system of parallel strips, set edgewise and notched or crozed on the under side for half their depth so as to allow of free circulation. For instance, the strips may be 2 × 4 in. or 2.5 × 5 in. with notches 4 or 5 in. long and 4 or 5 in. apart; the strips themselves are nailed down 2 or 3 in. apart. A similar effect is produced by continuous 2 × 2 in. strips laid parallel and resting on similar but short pieces 6 in. apart, laid crosswise on the bottom with spaces between their ends; or the parallel strips may rest on short blocks through which the nails pass.

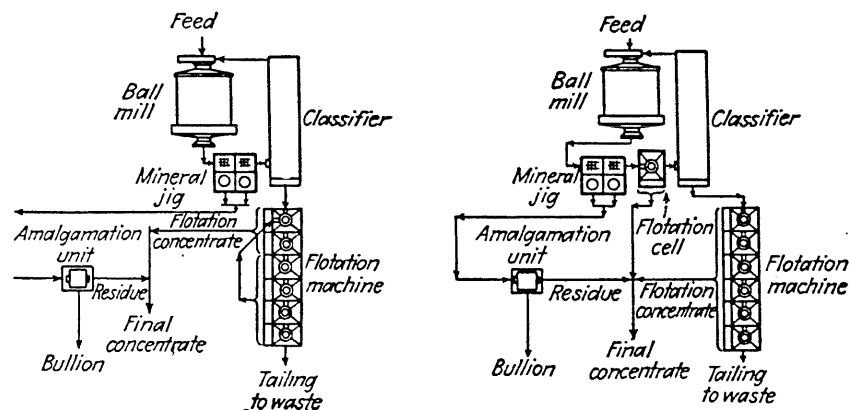
Upon the strips is laid a circle of coconut matting, sewn and hemmed, and fastened on the ring by occasional nails or staples. Over this is the filter proper, of heavy canvas, cut somewhat larger than the tank bottom, tightly stretched, and fastened by driving an inch rope into the recess round the tank bottom. In South Africa, hessian (burlap or hop cloth) has been laid on the wood grid, and coconut matting above this. When vats are discharged by shoveling, the upper cloth must be protected by boards, say 6 in. wide and a few inches apart, or by wider boards with numerous holes 1 in. or larger.

Around bottom discharge doors a tight wood ring is built up, of the same height as the filter. Near solution outlets all approaches must be kept clear. Near such outlets it is well to have a movable false section of bottom, which can be lifted occasionally to remove accumulated fine sand which may pass through holes in the filter. The

canvas filter should have a valve or opening, which can be closed by tying a sleeve sewn into it, to release air when the water is introduced.

Discharge Openings for Sand Residues.—These may be placed in the bottom of the vats or in the sides close to the filter bottom. In the latter case some of the hoops or rods for wooden vats must pass round the gate frame, or connect with the frame. Sluicing gates in the bottom should be near the sides, with one in the center of a large vat; for shoveling they should be so distributed that each serves a nearly equal area, but they should also be placed in straight lines so grouped as to require a minimum number of car tracks or sewers beneath the vats.

Side doors are rectangular; bottom doors may be round; they open outward and are conveniently hinged, and secured when closed by swing bolts or by a hinged lever arm tightened by a swing bolt. They may be of pressed steel or cast iron, made tight by square packing. A convenient center gate is that of Merrill, closing tight on



FIGS. 11-12.—Typical flow sheets of successful gold-milling installations:¹ 11, a simple flotation plant with a jig recovers metallics in the grinding circuit; 12, the jig recovers non-floating minerals, and the unit flotation cell following it recovers a coarse bulk concentrate and reduces slime losses.

an iron ring, and lifted from above by a threaded central rod in a column of pipe; the latter may also serve as support for a movable Butters distributor. To diminish resistance in lifting, such bottom valves should be made with the top an acute cone.

Leaching vats may be filled with current mill pulp, or with dam sand, conveyed by water or solution, or with dry sand or crushed ore. The main consideration is to secure uniform distribution and uniform permeability. If loaded wet, the vat should be first filled, or at least partly filled, with water or solution.

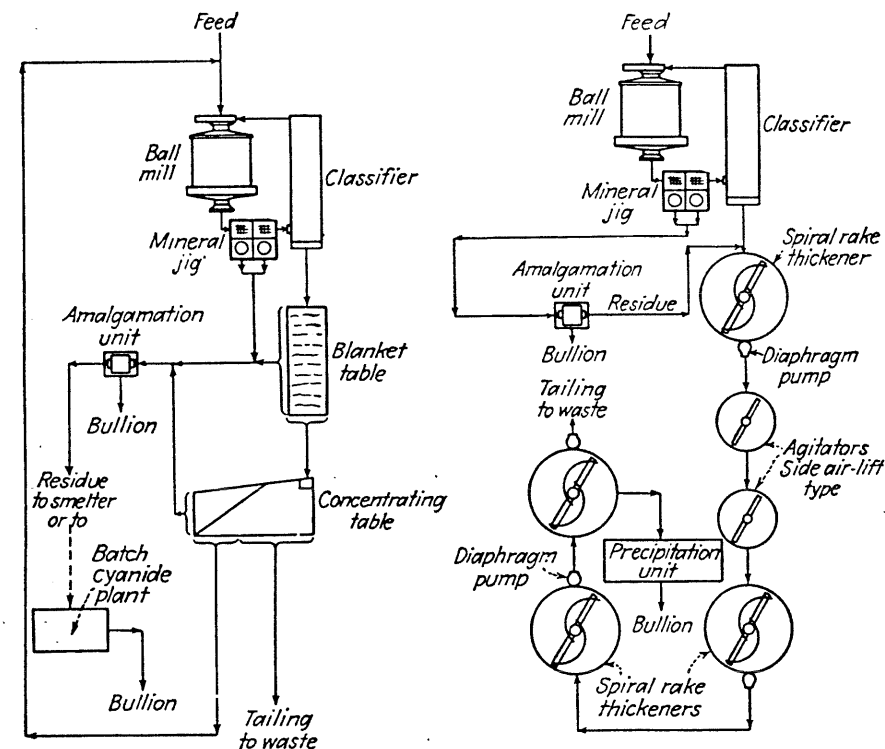
The total overflow during filling = original water + conveying water - interstitial space in charge = original water + total volume pulp fed - net volume of sand in charge.

Wet sand is usually fed through a Butters-Mein distributor (the revolving lawn-sprinkler type) with six or eight arms of 1½- or 2-in. pipe of differing lengths ending in elbows with flattened lips. For uniform filling the tank bottom is divided into equal annular areas, each radial pipe terminating nearly over the middle of a ring. The overflow is carried off by an annular launder, usually outside the staves, but sometimes built inside. With cheap labor, as in Africa and Mexico, filling was often done by a man with a hose.

¹ These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

As soon as filled, the sand is allowed to drain, and solution is applied to the top; it may be applied as a spray or allowed to pour upon the sand—in the latter case sheet-iron pans are used to prevent washing holes in the surface.

In filling with dry or drained sand, conveyers may be used—a main belt running along or between rows of vats, with a traveling shuttle belt across the vats—with automatic discharge. Or the feed may discharge over the center of the vat and slide down a radial inclined shoot with adjustable openings, the shoot being gradually



FIGS. 13-14.—Typical flow sheets of successful gold-milling installations:¹ 13, a small batch cyanidation plant may be used to obtain all-bullion products; 14, a jig removes coarse gold ahead of cyanidation, improving recovery and eliminating erratic tailings.

moved round the vat by hand. Or barrows, cars, etc., may be simply dumped over a coarse grating supported just above the top of the vat.

When filling with dry or drained sand, some hours of treatment time may be saved by simultaneously introducing solution below the filter bottom, so that it rises through the sand about as fast as the sand accumulates. As soon as the vat is filled and solution reaches the top, the bottom supply is cut off and normal downward leaching is started.

Direct treatment in the same vats in which sand is settled wet is only practicable when colloids are absent or have been washed out almost completely by cones, *Spitzkasten*, or other classification systems. Filter-bottomed collecting vats are sometimes used, and may be superimposed above the treatment vats, the settled sand being transferred to the latter by shoveling or by an excavating machine, such as the

¹ These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

Blaisdell. Instead of an annular overflow launder for the collecting tank, vertical slots have been used in Africa for overflow water outlets, the outflow level being automatically raised by roller-blind devices carried on floats, or it may be raised by cast-iron rings placed above a bottom opening.

In double treatment, the sand is collected and drained in such tanks, and given a preliminary cyanide solution treatment to displace the water; it is then transferred to the treatment vats below, where leaching is completed. The aeration thus secured is beneficial.

Caldecott's continuous-collecting system for sand consists in classifying with diaphragm cones and draining the thickened sand on a slowly revolving horizontal table, about 20 ft. in diameter, provided with a wide annular filter of coco mat and calico supported on wire screen. Here the sand is dewatered by a vacuum of about 5 lb. per sq. in. and removed by a fixed plow; it falls on a belt conveyer and is conveyed to the treatment vats.

Leaching.—The manner of applying solution varies. Gold dissolves rapidly, especially from fine sand, giving rich effluents in the early stages of leaching, the value falling off rapidly; silver often dissolves slowly, showing less difference in the value of the effluents with time. For instance, a particular ore yielded 70 per cent of the extractable gold, but only 35 per cent of the extractable silver in the first quarter of the total effluent solution. Hence, by precipitating only the first half of the effluent, and using the later portions fortified in cyanide for the early treatment of succeeding charges, the volume precipitated is minimized, so that it may be possible to make good extractions while precipitating not more than half a ton of solution per ton of sand.

The strength and the alkalinity of solution and the number of hours of contact must be determined to suit each case, and great saving may result from adjusting these conditions, and the degree of comminution of the ore, after the general treatment has been established.

When two solutions are used, the strong is generally applied first, and the weak is followed by wash water sufficient to displace it. The wash water and water in moist or water-crushed ore mix with the solutions to some extent, yielding "first and last drainings" of low NaCN content and low in precious metals. To preserve the volume of plant solution constant, these drainings, or low solution, are best precipitated separately and the barren run to waste. A slight saving is effected by using a buffer of this barren solution just before the wash water. Sometimes a little weak solution is similarly used before the strong; this is advisable if cyanicides have not been removed previously.

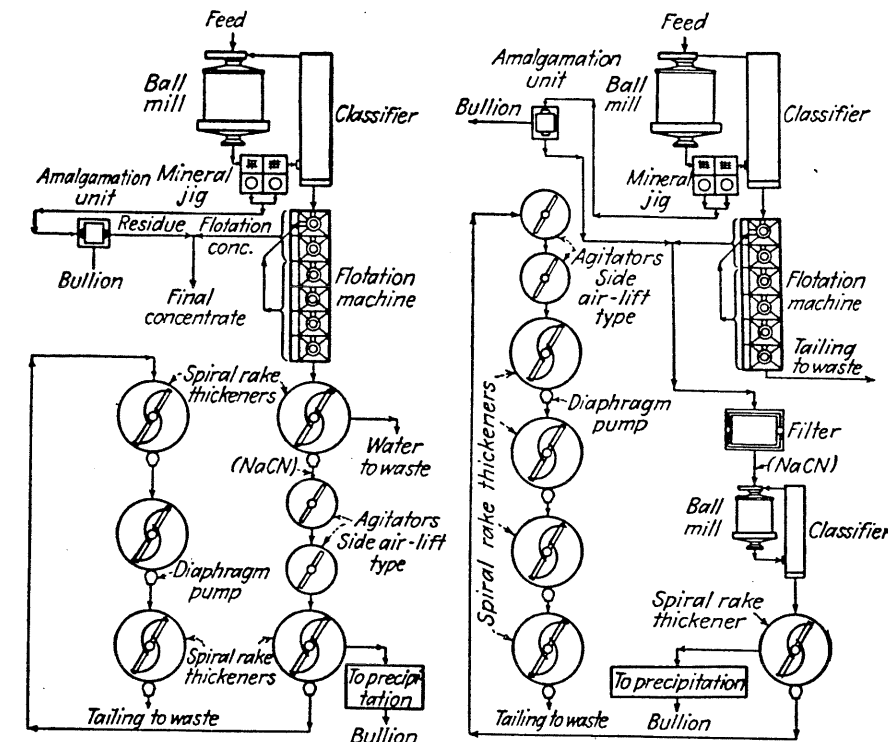
When dry ore is crushed in cyanide solution, the final wash water must be regulated to make up the deficit in solution that would occur otherwise.

The "leaching rate" of sand is measured by the fall per hour in the surface of solution standing over a charge of saturated ore in the vat. Good extractions are usually obtained with leaching rates of 2 in. or more per hour; at 1 in. more care is necessary, and slower rates are generally dangerous, shortening the time of contact by reason of the longer washing period necessary. As the voids in settled sand are usually about 50 per cent of the volume, solution descends through sand at about double the surface leaching rate, and the hours required for displacement of solution by wash water may be approximated by dividing twice the surface rate into the inches depth of charge.

With sand of given character, the leaching rate is not much retarded by a moderate increase in depth; the effect of depth is largely offset by increased head. An extremely thin layer of slimy material may, however, affect the rate profoundly. Application of a vacuum beneath the filter bottom was formerly practiced, when classification was

usually imperfect; while increasing the flow it tended to cause packing of the charge and lower the normal leaching rate; it may be used with advantage in the final washing stages.

Solution may be supplied continuously to the charge, or may be added at such intervals as to allow the surface to become drained and thus entrap air. Solution is sometimes circulated repeatedly through a charge by an air lift or pump returning it from the bottom to the top; this gives the desired aeration, but the ultimate removal of precious metal is retarded. Maceration or soaking by closing solution outlets for



FIGS. 15-16.—Typical flow sheets of successful gold-milling installations: 15, combination flotation and cyanidation permits milling both oxides and sulphides; 16, cyanidation of flotation concentrates produces all bullion.

long periods is an obsolete practice, but a too rapid flow should be controlled to avoid precipitating unnecessary solution.

Tanks.—For economy of material a round tank of uniform thickness should have a depth equal to one-half the diameter, for economy of hoops the shallower the better, for economy of foundation the reverse. A common compromise is to make the depth one-fourth to one-sixth the diameter. In steel vats the bottom is usually at least $\frac{1}{16}$ in. thicker than the sides; these also may be lighter toward the top. Steel tanks are riveted and have a ring of angle steel surrounding the bottom; a similar ring is often used at the rim, and deep tanks may be stiffened by a ring of T iron or a channel section round the middle. For wooden tanks, round iron or steel hoops are preferable to flat ones, which often develop rust on the underside.

¹ These flow sheets furnished by the Denver Equipment Co., Denver, Colo.

To get the full strength, the ends should be suitably upset before threading, and the section at the bottom of the thread considered in calculating strength. For sizes requiring over $1\frac{1}{8}$ -in. round it is preferable to use $1\frac{1}{8}$ -in. or larger square steel. The sizes may increase by $\frac{1}{8}$ from $\frac{1}{2}$ in. at the top, and the spacing be made correspondingly closer as depth increases. Heavy hoops and rings must be rolled to the proper curvature before use, and hoops must be provided with properly designed couplings.

In calculating the necessary cross section of hoops or thickness of side, wet sand, like slime pulp, must be considered as a perfect fluid, as there are times when it is dangerously near that condition. Settled sand may be assumed to have 50 per cent voids, when the specific gravity of the wet mixture p is $0.5(d + 1)$ where d = specific gravity of dry sand.

D = diameter of tank in feet.

H = depth from top to center of ring (or hoop) considered, in feet.

p = specific gravity of pulp [= $0.5(d + 1)$ for wet sand].

t = thickness of steel vat in inches at depth H .

W = inches width of ring controlled by hoop in wood vat at depth H .

Strain on square inch cross section of steel sheet = $\frac{2.6DHP}{t}$ lb.

Total strain on cross section of hoop = $2.6WDHp$ lb.

Thus, with a steel tank 50 ft. in diameter, the metal $\frac{1}{4}$ in. thick at a depth of 10 ft., when filled with wet sand of specific gravity 2.8 ($p = 1.9$), stands a strain of

$$2.6 \times 10 \times 50 \times \frac{1.9}{0.25} = 9880 \text{ lb. per sq. in.}$$

Similarly with a wooden vat under the same conditions, a hoop 10 ft. from the top, spaced 6 in. from adjacent hoops, is subject to a strain of

$$2.6 \times 6 \times 10 \times 50 \times 1.9 = 14,820 \text{ lb.}$$

and for a factor of safety of 5, the hoop must be capable of standing 74,000 lb.

Leaching in the Filter Press.—This includes collection and complete treatment in the press, and usually requires solution to be applied under a pressure of at least 30 lb. per sq. in. Separated slime or all-slimes ore, suitably thickened, is fed into the press by gravity, monte-jus, or pump, until filled. Alternate plates are then connected with compressed air and the water displaced. Solution is next applied through the same channels, and leaching (which may involve several solutions and may be alternated with air treatment) is continued as long as gold dissolves; it is then displaced by wash water, and the solid is finally discharged.

The Dehne press, used in Western Australia for roasted ore and in some cases for raw slime, was opened and discharged by hand; it did not differ essentially from the ordinary plate-and-frame press. Treatment was completed in some cases in a 2- or 3-hr. cycle, but operation was expensive, even when opening and closing were effected by hydraulic power, and it was generally found preferable to dissolve the gold in agitators and use the press for filtering and washing only.

The Merrill press discharges the solids by mechanical sluicing through a bottom channel provided with ports, making it possible to use a press continuously for many months without opening or changing cloths. Sluicing is effected by a series of nozzles in a rotating pipe or bar running the full length of the press and requires 3 to 5 tons of water per ton of solid, depending on the character of the latter; much of this water may be recovered, if desired, by a thickener or rotary filter. While the first cost of this filter is comparatively high, the treatment requires a minimum of labor. With granular slime, a 4-in. frame is suitable; if extremely fine or flocculent, a 2- or 3-in. cake is preferable. Center washing may also be used, in which case the cake is not

made to fill the frame completely, and air and solution are applied through the central opening in each cake instead of passing crosswise through the frame. In this case the cake is loosened by applying air for a short time behind the cloths prior to sluicing.

Leaching in the press is essentially similar to gravity leaching of sand, but much more rapid, occupying hours instead of days. For instance, with Homestake ore, the coarser mill sand yielded 70 per cent of its gold by leaching in a 7-day cycle; if reground this yield increased to about 80 per cent, the finer portions of the sand yielding 90 per cent. The slime and fine sand treated in the Merrill press yield 90 per cent in a cycle of 8 to 10 hr., of which 1 hr. is consumed in filling and one in sluicing. The operating cost in each case is about the same.

The Sweetland press has a cylindrical shell, opening by a hinge, the circular plates being tipped for discharge.

Simple Decantation.—In this process of slime treatment the material was agitated with cyanide solution and allowed to settle; the clear supernatant liquid was decanted off by a swinging pipe or flexible hose supported by a float that kept the inlet near the surface. This liquid was replaced by barren or low-grade solution or water; mixing, settling, and decantation were then repeated, and the same cycle might be repeated several times. The first decantate was always precipitated, sometimes the second or third, and the barren solution used with later decantates or washes for the make-up on a succeeding charge. The thickened residue, including more or less low-grade solution, was finally run off to a dam, or in some instances filtered. Some liquid separated on the dam and was sometimes pumped back for use in washes.

Successive agitations were carried out in the same vat—using mechanical agitation often aided by air—or, in a series of vats, one for each stage. In the latter case time was saved by hydraulicking the settled slime with solution or running it by gravity into a vat already containing solution, or, if the vats were on a level, a centrifugal pump was used with arrangements for drawing in a certain proportion of air for oxidation. Lime was commonly added to facilitate settling.

The process was adaptable to existing shallow vats by addition of an arm or paddle agitator. In South Africa, large shallow vats were used with bottoms slightly coned, but it was found that, with increased depth, air agitation could be advantageously substituted, and this led to the development of the extremely deep Pachuca tank by F. C. Brown at Komata Reefs, New Zealand, in 1902.

The Pachuca may be $10 \times 30 \times 45$ ft., with a central air lift one-tenth the diameter and a cone bottom inclined 60 deg. In addition to the lifting air, a second small pipe was added for stirring settled slime, and later a spider or movable set of radial pipes surrounding the air lift for the same purpose. The air outlets were valved or covered with flexible rubber to prevent entry of slime when the air was cut off.

At Waihi the Brown vat was used for crushed ore in connection with the Moore filter; at Goldfield and Treadwell it was used for fine-ground concentrate, and the final removal of solution was effected with a Kelly filter press.

Continuous or series treatment (not to be confused with countercurrent) was first used by Grothe and Mennell in 1908. The cyanide pulp is transferred through a series of three to six Pachuca tanks, maintaining it in agitation, thus saving the time occupied in emptying and filling, settling and stirring, and avoiding loss of head, except a few inches between successive tanks. The connecting pipes between adjacent tanks are set at a downward angle of about 60 deg., with an intermediate section of rubber hose. After leaving the agitation system the pulp passes to a suitable filter, an intermediate storage tank being usually provided in advance of the Moore and Butters filters, which have been much used. This is unnecessary with rotary filters, which are automatic and almost equally effective.

By keeping the outlet at a suitable distance from the surface, any considerable accumulation of sand is prevented; a certain accumulation of sand in the system is desirable, giving the coarser particles a longer treatment time than the average. Shallower agitators, as the Dorr, Trent, or Parral, may be used; the discharge may also be selected by other means. Short circuiting of some particles must inevitably occur, but in a series of tanks the probability of this is decreased.

The intermittent vacuum filters (Moore, Butters, etc.) and pressure filters (Burt, Kelly, etc.) require more attention, but are more flexible in application, as treatment can be completed in them, as well as washing and dewatering; rotary vacuum filters (both the drum type, Oliver, and Portland, and the American or disk type), are practically restricted to washing and dewatering. Dewatering may be carried by any of these filters to about 25 per cent moisture.

In the Kelly system the agitators are followed by two sets of rotary washing filters in series; the cakes discharged from the first set are repulped with wash solution or water in intermediate mixers to a liquid ratio about 1:1. The loss of dissolved value in the final cake is thus minimized.

Continuous countercurrent decantation, an adaptation of a well-known principle,¹ was attempted in cyaniding by Randall (South Dakota) in 1901 and by Denny (South Africa) in 1903, using cone-shaped agitators. It was made a practical success by the application of the Dorr thickener, a series of three to five of these being used, together with a number of agitators, the ore being usually crushed in solution.

After leaving the first thickener, the partly thickened pulp passes through the group of agitators, which may be in series or series parallel, and then through the remaining thickeners, and is discharged with or without filtration. By setting the last thickener highest, and the others in steps leading to it, the decanted solution flows back by gravity in the opposite direction to the solid, while the thickened pulp is transferred by diaphragm pumps. If on a level, the solution may be moved by air lifts. Excess solution from the first thickener is precipitated and returned to the second or third one from the end; cyanide is added to one of the agitators.

Points essential to success are solution of the maximum gold or silver before leaving the agitator system and efficiency of settling in succeeding thickeners, to at least 50 per cent solid if possible; in most cases, and always if the percentage of solid in effluents is under 50, the final discharge should be treated on a rotary filter to reduce soluble losses. Underflow solution is always slightly richer than overflow, owing to some dissolving and to diffusion of adsorbed or absorbed solution.

The flow sheet of United Eastern mill shows conditions prevailing with a pulp difficult to settle. Theory and practical applications are discussed by Eames,² Dorr and Dougan at Elko Prince,³ and W. O. North at United Eastern.⁴

¹ The countercurrent principle allows the original ore to be treated with solution fairly rich in precious metal, but when partly exhausted, it must come in contact with poorer solutions, finishing either with wash water or with solution carrying only traces of value. The valuable content of the reagent should be as closely as possible proportioned to that extractable from the ore it meets.

An approach to this ideal is the conveying of crushed ore through a launder or horizontal pipe while a slow stream of cyanide solution travels in the opposite direction. Mere prolonged agitation, or the continuous passage of pulp through a series of agitators without a countercurrent, is entirely opposed to this principle, the solvent becoming enriched as the ore is impoverished.

In any continuous system the time an average particle remains in any thickener or agitator is found by dividing the weight of pulp passing hourly into the total weight of pulp contained in that unit. The arrangement (series or parallel) of any group of units does not, therefore, affect the average time occupied by the pulp in passing the group. Lengthening out the series of units decreases the probability of the rapid escape or short circuiting of any particle. (Cf. pp. 181 to 184, of the volume entitled "Principles and Processes.")

² *Trans. A.I.M.E.*, Vol. 57, p. 142.

³ *Ibid.*, Vol. 60, p. 84.

⁴ *Ibid.*, Vol. 68, p. 548.

Residues may be discharged by sluicing where water is plentiful, and in some cases carried off by convenient streams, but more commonly require to be settled in dams. In some localities substantial dams must be built of concrete or masonry, or heavy timber, but it is more usual to construct the dam from the coarser portion of the tailing itself. Sometimes empty cyanide boxes or drums are filled with sand to form the initial wall, or cells of light woodwork are similarly filled, or the tailing itself is shoveled up to form a retaining wall. The sluiced tailing is then roughly classified in such a way as to deposit the coarser material near the dam wall, while the finer settles nearer the middle, where a steeply inclined or vertical overflow box may be arranged, the overflow level being gradually raised by adding slats when necessary. Where possible, it is convenient to have two or three dams or sections, one of which may drain and consolidate while another is in use, the more solid portion being then shoveled up to form the wall. A fair proportion of clayey material, or of contained lime, makes an excellent binder for the heavy sand, so that such dams may be built up on suitable slopes to a great height.

Sand residue may be removed by shoveling through bottom doors or by a mechanical excavator, such as the Blaisdell, and carried off in cars, or by aerial conveyers, or by a conveyer belt which may deliver it to an elevating stacker. Slime, dewatered by a rotary or other filter, may be similarly carried off.

Or the tailing, sluiced or in cars, may be used for filling the stopes from which it originated; if more than a trace of cyanide remains, it may be necessary to decompose it by addition of permanganate.

Slime residues, thickened or settled without a filter, may usually be conveyed in pipes, but require a large area for satisfactory collection.

Watercourses below residue dams are liable to contamination sufficient to cause the death of birds and animals unless due precautions are taken. Whenever possible, it is desirable to pump any accumulated liquid back to the plant as a matter of precaution, as well as of economy on account of contained cyanide and precious metal.

"Dissolved values" carried to residue dams behave differently according to climatic conditions. In arid regions, evaporation takes place rapidly and salts effloresce at the surface, forming a thin layer of much enriched material—in some cases worth \$100 per ton—which may be collected from time to time by careful sweeping or scraping, and returned to the plant. Where the rainfall is fairly heavy, the surface is usually impoverished; in some cases reprecipitation takes place on organic matter near the floor of the dam, in others some recovery may be made by precipitating the seepage by zinc boxes or, if acid, by scrap iron.

Similar dams may be used for the storage of untreated tailing intended for subsequent treatment. These should be constructed with a view to the reclamation of the tailing, removing trees and other obstructions, leveling the bottom, and excluding organic matter when possible; sand and slime may advantageously be segregated.

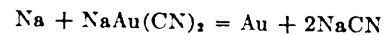
PRECIPITATION

Electrolysis as a mode of precipitation attracted many inventors as it seemed reasonable to expect a large measure of regeneration. Siemens & Halske used multiple iron anodes and thin sheet-lead cathodes, which were to be removed and cupeled after accumulating a suitable amount of gold; the current was of low voltage and a density of 0.04 to 0.06 amp. per sq. ft. The iron anodes were encased in hessian (burlap), but much Prussian blue and other by-products complicated the process, and the loss of iron was 0.3 to 0.5 lb. per ton treated. The main difficulty was the excessive electrode area and tank volume required approximately to exhaust a solution, the electrodes being 1 to 1.5 in. apart and 20 sq. ft. or more in area.

Butters modified the process by using tinned iron cathodes and much higher current density; Andreoli invented anodes of lead coated with lead peroxide; Cowper-Coles used anodes of peroxidized lead and cathodes of aluminum, from which the deposited metal was to be stripped in sheets.

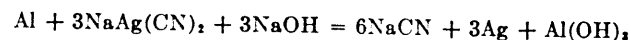
Several inventors attempted to precipitate the gold as an amalgam by using as cathode a layer of mercury or an amalgamated copper plate. Some filtered the solution, others attempted to precipitate on plates suspended in the pulp during agitation; some added common salt to increase the conductivity, but in no case was entire success attained. Pelatan and Clerici introduced several apparatus for this purpose, and others were devised by Riecken, Hendryx, Oliver, Mumford, Hebaus, and Noriega.

Sodium and Sodium Amalgam.—The ideal precipitant for gold and silver from cyanide solutions would be metallic sodium, completely regenerating the alkaline cyanide:



Attempts to use this reaction by means of sodium amalgam have not met with practical success. Molloy proposed to make metallic sodium by electrolysis of Na_2CO_3 solution with a mercury cathode communicating with and diffusing into a body of mercury kept in contact with the cyanide solution; others sprayed sodium amalgam through a rising stream of solution, or kept it moving by means of amalgamated disks.

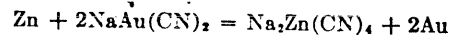
Aluminum and zinc stand next to sodium in the line of available positive metals, and have proved the most practical precipitants for gold and silver. Each replaces silver in solution, but aluminum forms no double cyanide and requires the presence of some free alkali. The equation



indicates the complete regeneration of NaCN and the formation of alumina, which, however, dissolves in NaOH to form an aluminate, which may be assumed to be NaAlO_2 . The NaAlO_2 reacts with CaO in solution to form insoluble CaAl_2O_4 . Gold is not readily precipitated by aluminum, unless a fair proportion of silver is present; mercury is, precipitated but copper is not.

Aluminum dust has been successfully used in silver mills at Cobalt; it is fed in a manner similar to zinc dust, but must be retained in a special agitating tank to increase the time of contact. Hamilton's system, in use at Butters' Divisadero plant, involves the removal of calcium by a minimum of soda ash prior to adding aluminum, the aluminum passing into solution being later thrown out by lime used in the mill. Hamilton states that, in practice, 1 part of aluminum precipitates only 3 of silver in place of the calculated 12, the difference being mainly due to a reaction with NaOH to yield hydrogen. Alumina in the precipitate makes refining difficult.

With zinc, the essential reaction is, similarly, a replacement of gold and silver, the zinc going into solution as double cyanide:



No regeneration is apparent, but the double cyanide thus formed has a marked solvent action on gold and silver, which is increased by the presence of free alkali up to a ratio of about 4NaOH for each molecule, or about two and a half times the weight of zinc. Precipitation is complicated by side reactions, especially the evolution of hydrogen by reaction of Zn with NaCN and NaOH forming additional $\text{Na}_2\text{Zn}(\text{CN})_4$ and Na_2ZnO_2 (zincate); this H further reacts to form sulphide by reduction of NaCNS and other sulphur salts, the Na_2S then precipitating Pb, Hg, or Ag as sulphide instead of metal. Some precipitation of Hg, Cu, etc., is due to direct action of zinc. Christy and others

have written equations purporting to show a definite proportion between Au and H produced, but there is no fixed relation.

Zinc shaving was recommended by MacArthur and Forrest for a "metallurgical filter" after testing various forms of zinc. U. S. patent 418138 (1889) describes a vessel or series of vessels, with perforated false bottoms, carrying a sponge of "filiform zinc" cut by turning tool from a series of zinc disks, solution being arranged to rise through each section of a set of boxes or compartments.

Zinc boxes are made of wood or steel, occasionally of cement, sometimes in units but usually in a series of five or six similar compartments, each with a false screen bottom, the new zinc being added at the lower end and moved up as it disappears from the upper end. Each section usually has a plugged bottom hole communicating with a pipe or enclosed launder which leads to a tank or receiver for use at the cleanup; the top is often covered with coarse screen as a precaution against theft. At a cleanup, the fine material is shaken down and washed through the screen bottom, and drawn off or washed down to the receiving tank, from which it is pumped to a small filter press. A considerable amount of precious metal is held back by the residual zinc moved to the head compartments. Some "short zinc" often has to be separately treated. It is advantageous to increase the space beneath the false bottom of the head compartments. The actual zinc-filled space usually recommended is 1 cu. ft. for each ton of solution daily precipitated, but in practice it may be one-quarter to double this. Five compartments are usually sufficient, but it is advisable to keep an empty compartment at the tail end.

Suitably packed, a cubic foot of fine zinc shaving weighs about 6 or 7 lb., but the coarser material used for silver may weigh 14 lb. It is now made by soldering together sheets of rolled zinc and coiling this closely on a roller or mandrel, which is then set in a lathe and cut by a chisel making an oblique cut at the ends. It is desirable when cutting to wind the thread into hanks of a size to fit the boxes in which it is used.

If the shaving is assumed to be a continuous rectangular strip of width α and thickness b in., the surface exposed by 1 lb. of zinc is

$$0.055 \left(\frac{1}{\alpha} + \frac{1}{b} \right) \text{ sq. ft., or nearly } \frac{0.055}{b} \text{ if thin}$$

If the section is not rectangular, but a parallelogram of angle A , this must be multiplied by $\text{cosec } A$.

Zinc dust as a practical gold precipitant was first used by Sulman at Deloro, Ontario, added intermittently to a rising stream of solution in an inverted cone, and passing to a filter. Later Waldstein and others added it by sprinkling it dry or as an emulsion in large charges upon vats of solution in a state of agitation, which was then pumped through square filter presses. Merrill introduced the practice of feeding it continuously to a moving stream of solution and using a triangular filter press; this system is now in use at nearly all the larger plants on the American continent, and is gradually displacing shavings elsewhere.

Feeders of several types are in use. One of the best is a slow-moving horizontal belt, on which a charge sufficient for several hours is spread in a uniform layer; this falls into a small mixing cone through which a trickle of auxiliary solution conveys it to the pump suction pipe. Another is a hopper at the outlet of which revolves a roller or pulley which removes a narrow ribbon of dust, the thickness of which is regulated by an adjustable slot. Or the zinc may be removed from the hopper by an augerlike horizontal screw. These feeders require a jarring mechanism to prevent the dust from adhering or bridging. Sometimes a miniature tube mill is added as a mixer. For accurate measurement it is convenient to have duplicate tanks of 100 or

200 tons capacity, which are precipitated alternately, but a large single tank may be pumped continuously while solution flows into it.

Abandoning air agitation effected a considerable saving of zinc, but the most marked improvement in precipitation has been the Crowe process of removing air from the solution by passing it through a vacuum tank on its way to the pump and just before introducing the zinc. Percolation through sand clarifiers containing some finely divided iron and pyrite has been recommended. In precipitating gold, the practical minimum of zinc dust is now between 0.1 and 0.05 lb. per fluid ton, or 25 to 50 parts of zinc per million of solution. When starting a press after a cleanup, it is advisable to add 50 per cent or more dust in excess of the normal charge; this is gradually diminished in successive charges until the regular amount is reached.

If zinc dust consists of equal spherical particles of diameter d in., 1 lb. exposes a surface of $0.165/d$ sq. ft., and contains $7.544/d^3$ particles. At an average diameter of $1/10,000$ in., 1 lb. exposes 1650 sq. ft., and 0.1 lb. spread through a ton of solution gives some 13,600,000 particles to the cubic inch.

For complete reaction 1 unit weight of Zn precipitates 6.03 units Au, 3.30 Ag, or 1.93 Cu, but the efficiencies obtained in practice are often extremely low, sometimes only a fraction of 1 per cent with low-grade gold solutions; with rich silver solutions 50 per cent may be reached, if complete exhaustion of the solution is not aimed at. Gold solutions can usually be precipitated with zinc dust to within 1 cent per ton, with less expenditure of zinc than shavings require.

The best zinc dust was formerly imported; it usually contained about 2 per cent lead and often some cadmium; a much more efficient dust is now made in the United States, practically free from foreign metals and extremely uniform in size, the finer grades nearly all passing a 300-mesh sieve. It invariably contains oxide, often between 5 and 10 per cent ZnO, but this is not visible under a microscope, which shows uniform bright spherules. The thickness of a surface layer of 10 per cent ZnO on spheres would be less than one-fiftieth the diameter. Extreme fineness is advantageous with low-grade gold solutions, but not necessary with the higher metal concentrations obtained from silver ores.

With zinc dust, 1 sq. ft. net filter surface suffices for 1.5 tons (or 50 cu. ft.) solution per day, or 6 tons per hr. per 100 sq. ft.; with clear solutions a press may be run for long periods at double this rate. Colloidal suspended matter soon increases the pressure and reduces the pumping rate. For gold solutions 2-in. distance frames are suitable, 3- or 4-in. for silver. On opening a press most of the cake falls into the wheeled tray placed beneath; the remainder is easily removed by scrapers.

The practical efficiencies obtained with zinc dust, and the accumulations of zinc in solution, have averaged about the same as with shaving.

The dust process involves a more expensive installation than zinc shavings, but has the advantage of greater compactness and cleanliness, and involves less labor in maintenance and cleaning up as well as less risk of theft. The periodical cleanup is absolute, while a holdover of several thousand dollars' worth of precious metal commonly occurs with zinc shavings, and makes it impossible to compare the actual with what is often called the "theoretical" recovery. After a destructive fire, precipitate in a filter press has been found intact, while zinc boxes have entailed great difficulty in the attempts to recover their contents. At a gold plant a press occupying a floor space of 5×14 ft. can easily carry a month's accumulation of \$40,000.

The comparative cost of the two systems at any time depends, of course, upon the wage scale and the relative prices of zinc dust and spelter. The Crowe process effects an economy in both.

Zinc in other forms has occasionally been used as a precipitant, such as small disks, slugs, or balls in a rotating cylinder or pan through which solution passed.

Sodium sulphide, Na₂S, does not appreciably affect gold or copper in cyanide solution, but precipitates silver as Ag₂S from NaAg(CN)₂, at the same time regenerating NaCN and carrying down some gold in the presence of a large proportion of silver. Owing to the reversibility of the reaction, either precipitation must be imperfect or a slight excess of Na₂S must remain in solution, which is an objection to its use, as is also the necessary further treatment of the precipitate. It was patented by Janin and Merrill in 1894, but was not used until adopted at Nipissing as a substitute for the expensive aluminum dust. The precipitate is here reduced to metal by the Denny process, by contact with slugs of aluminum in a tube mill.

* **Carbon as a Precipitant.**—Graphite has no precipitant action whatever on gold or silver in cyanide solution, nor has wood fiber (cellulose). Charcoal, partly burned or charred wood, some varieties of decaying wood, and some of the carbonaceous material found in certain black or "graphitic" shales and slates, all precipitate gold from its solutions, some of them rapidly, and in some cases they may prevent its solution. Freshly burned charcoal is most energetic; after long storage it is much less effective, but the precipitating property may be largely restored by reburning. It is usually assumed to be due to occluded gases (CO or H), but nothing has been definitely determined on this point; these gases and the hydrocarbons in their ordinary form are quite inert. Coke and some varieties of coal have some precipitating effect, and in South Africa Caldecott patented the use of partly burned coal as a precipitant. In Australia, charcoal has been used to some extent as an actual precipitant, but the large volume required makes it inconvenient, and the final recovery of the gold is troublesome. Silver also is less completely precipitated.

The discovery, during the First World War, of means of activating charcoal, and the known high activity of coconut shell and other dense charcoals, and of kelp char, and the fact that fresh pine charcoal is almost equally effective as a gold precipitant, all suggest that charcoal has some practical possibilities if a better mode of application is discovered. Agitation with finely powdered, recently burned charcoal followed by filtration gives promising results on the small scale.

Edwards at Yuanmi, Western Australia, used three Butters-type vacuum filters in series, each of 260 sq. ft. surface and charged with 300 lb. of ground charcoal; this system precipitated 280 to 420 tons daily, leaving 7 to 8 cents gold in solution out of an original \$3.25. One filter was renewed every three days, making consumption 14 to 13 lb. per ton. The dried product was burned and the ash fluxed in crucibles with borax, sand, and salt.

Refining.—Dry cyanide precipitate may contain up to 70 per cent metallic zinc or ZnO; that obtained by zinc dust from gold ore averages about 25 to 40 per cent, that from rich silver ore much less. If precipitant and solutions were lead-free, precipitate from rich gold or silver solutions may be melted directly in crucibles with borax; it is more commonly acid-treated to remove zinc or sometimes roasted in iron muffles as a preliminary step. The removal of zinc by distillation in Faber du Faur furnaces has been used experimentally.

* Borax is the most important flux, best used as crushed borax glass; the crystals contain 50 per cent of water. Soda ash and silica are also useful, depending on the impurities to be fluxed off; bicarbonate is sometimes used in place of soda ash, though more expensive and less efficient. Niter or sodium nitrate may be used to oxidize zinc, sulphides, etc.; manganese peroxide may be substituted, as it gives off oxygen more gradually; oxidizing agents attack graphite crucibles, and also tend to carry silver into the slag. Clay liners may be used to protect the crucibles. Fluorspar helps to maintain fluid slags. Litharge is used only when cupellation is the final step in the refining process.

Lead present in zinc or added to solutions appears in precipitate as metal or PbS, and sulphuric acid removes but little of it. Acid treatment, if followed by thorough washing, removes most of the zinc and calcium, and part of the copper. It is carried out in a lead-lined tank with a mechanical agitator, water being first introduced and strong acid added gradually to prevent boiling over. A suction fan is necessary to remove fumes, especially HCN, H₂S, and AsH₃; and care is also necessary on account of the hydrogen evolved. When action ceases, more water is added, the liquid is decanted on a filter or through a small filter press, the precipitate is then transferred to the filter and washed and finally dried to a stage where it can be handled without dusting. Sodium bisulphate, NaHSO₄, a by-product of acid works, may be used as a substitute for sulphuric acid.

After acid treatment silica, cadmium, mercury, and some copper remain with the precious metals, and some CaSO₄ and ZnSO₄; mercury may sometimes be profitably distilled off after adding lime or metallic iron to decompose HgS. On melting with reducing agents sulphates are deoxidized, yielding matte, which usually carries silver, as well as copper, lead, and iron.

Large crucibles, up to No. 400, may be used in tilting furnaces fired with oil, gas, or powdered coal; sizes 100 and smaller may be poured with hand tongs from wind furnaces using coke, etc. Electric heating has been but little used. In direct fluxing the cost of graphite crucibles is a serious item; melting may also be done without crucibles in tilting furnaces lined with carborundum or other refractory, or large crucibles may be set on a reverberatory hearth.

Rich silver precipitate is, at large plants, fused directly on a reverberatory hearth and tapped to molds; at Nipissing it is finished on the hearth by air-blast refining. United Comstock has an oil-fired tilting reverberatory.

The Tavener process, developed in South Africa, consists in mixing the precipitate with litharge and some sand, and smelting in a small reverberatory or pan furnace; the reduced rich lead is tapped off and cupeled.

At the Homestake, precipitate, raw or acid-treated, is partly dried and briquetted after mixing with a flux of borax, borax glass, litharge, and a little silica. The briquettes are fused in a small English cupel furnace on a test of Portland cement (three-fourths) and limestone (one-fourth) which is started by adding a little lead; the slag is tapped off from time to time together with some of the reduced lead. When all melted the surface is cleaned off and the lead cupeled on the same test, returning accumulated lead; the final slab of gold is broken up while still hot, melted in crucibles, and cast into bars. Low-grade precipitate is best briquetted, passed through a small blast furnace, and the lead cupeled.

The cupel slag, matte, and similar by-products are treated in a small blast furnace, and the lead is either cupeled directly or used to start cupellation in the next run. The litharge from the lead processes is ground and used for flux at the next cleanup.

If the precipitate is briquetted and treated raw, the increased losses in lead in slag, etc., offset any saving in acid. The holdover in blast-furnace by-product lead and litharge is less than 1 per cent of a month's run, and the only by-product to be marketed is the impoverished matte from the blast furnace.

In fluxing, 100 lb. of raw gold precipitate may give up to 100 or even 200 lb. of slag; after acid treatment and lead refining, about the same total of slag and litharge together, but the proportions vary greatly with the flux and condition of the precipitate.

At all plants large enough to justify the expense—treating, say, at least 400 or 500 tons daily—a small lead blast furnace is an excellent investment. Not only can the by-products of cyanide cleanups—and if necessary the entire cleanup after briquetting it or setting it with some binder—be treated economically in such a fur-

nace, but all sorts of by-products can be handled at intervals with little or no previous preparation, such as mill skimmings, rich pyrite, black sand, iron superficially amalgamated, old copper plates, sweepings, rich slags, and crucible scrapings. An important essential is to avoid charging finely divided material, or the blast may become choked and the furnace freeze. Fines must be briquetted or set with some suitable binder, such as water glass or acid.

In preparing cyanide precipitate for refining by means of a cupel or blast furnace, the expense is about the same whether a preliminary acid treatment is used or not; the use of acid effects an important reduction of the lead losses. If much zinc remains in the mass smelted, the slags become stiff from the presence of spinellike compounds, and more lead must be left in the slag. If the washing of acid-treated precipitate is imperfect, sulphuric acid or sulphate of calcium or zinc remaining, the SO₄ becomes reduced in the cupel or furnace and matte is formed.

In many cases the mixture of by-products is almost self-fluxing, requiring only the addition of a little limestone or assay slag to run freely. Fluorspar is sometimes useful in maintaining a fluid slag. In the final furnace by-products, such as matte, slag, and litharge, the ratio of silver to gold is generally much higher than in the bullion bars.

Air and Oxygen in Cyaniding.—The oxygen necessary to dissolve gold is supplied by air dissolved in the solution, which is slightly less than that carried by an equal volume of water. Additional oxygen may be furnished in leaching by allowing the solution to drain low before adding more, and thus entraining air; sometimes air is blown for several hours at a time through the filter bottom after draining a charge, and it may be similarly blown through charges of slime in the filter press.

In slime treatment, air thus serves a double purpose, being used as a mechanical agent in agitation or air lifting, as well as to aid solution of gold; when transferring pulp by centrifugal pumps, air is sometimes admitted at suitable openings, and one of the advantages of the "double treatment" of sand is to admit air freely.

The oxygen required for actual dissolving of gold is small in quantity. Assuming the interstitial space in sand as 50 per cent, the solution contained in a ton of saturated sand (specific gravity, 2.6) would suffice to dissolve over 2½ oz. of gold or 1.5 oz. of metallic silver, were it not used up by reducing agents, but to oxidize these reducing agents (mainly ferrous and sulphur compounds in ore, or organic matter introduced) a large volume of additional air must be supplied. In precipitation, the presence of O is undesirable; see under Crowe Process (page 328). Deep agitators and pressure filtration favor the dissolving of O, while vacuum treatment removes it from solution.

Excessive use of air is undesirable, as it carries off some HCN due to hydrolysis of NaCN, but free alkali almost entirely prevents this. The CO₂ in atmospheric air also tends to decompose NaCN; the CO₂ in 1000 cu. ft. of free air at sea level will decompose about 0.1 lb. NaCN, or consume 0.06 lb. of CaO, yielding over 0.1 lb. of CaCO₃. It may be removed by washing the air with caustic soda or lime water. Accumulation of CaCO₃ on cloth gradually reduces its permeability; this is partially restored by treatment with dilute HCl, but each successive acid wash leaves the cloth a trifle less effective than the preceding. Air from compressors usually carries oil, which produces an objectionable coating on filter press cloths; this oil may be excluded by passing the air through a special filter press of a few large frames.

At sea level and freezing point, 1000 cu. ft. of dry air contains 18.65 lb., 8.6 kg., or 272 troy oz. of oxygen. But at ordinary ranges of temperature and atmospheric moisture, the O actually present is between 90 and 95 per cent of these weights; at higher altitudes, the weight of O per 1000 cu. ft. is directly proportional to the lower barometric pressure. It is convenient to read this by a mercurial barometer and to note that the pressure of a 1-in. column = 0.49 lb. per sq. in., also that the barometer falls about an inch for each 1000 ft. elevation from the normal 30 in. at sea level.

Barometer, inches mercury.....	30	25.0	20.0
Approximate elevation corresponding.....	0	5,000 ft.	10,000 ft.
Pounds per square inch.....	14.7	12.25	9.80
Relative solubility of oxygen.....	100	83.3	66.7

SOLUBILITY OF OXYGEN IN DISTILLED WATER WHEN EXPOSED TO AIR AT SEA LEVEL
(WINKLER)

Temperature, Centigrade.....	0	5	10	15	20	25	30
Temperature, Fahrenheit.....	32	41	50	59	68	77	86
Oxygen, cubic centimeters per liter ¹	10.2	8.9	7.9	7.0	6.4	5.8	5.2
Oxygen, milligrams per liter ²	14.6	12.7	11.3	10.0	9.15	8.15	7.6

¹ From an atmosphere of pure oxygen the solubility is about 4.8 times this. Nitrogen from air dissolves at approximately double these volumes.

² Multiply these weights by 0.002 for pounds O, and by 0.029 for troy ounces O, per ton of water.

For cyanide solutions, at sea level, it is safe to assume the solubility of O as over 90 per cent of that in water (Maclaurin found 87 per cent for 1 per cent KCN, 50 per cent for 10 per cent KCN) and at higher altitudes, to reduce this proportionately to barometric pressure. Thus at 5000-ft. elevation the maximum solubility of O in ordinary solutions may be taken as about 8 mg. per l., or 8 parts per million, which is about 0.23 troy oz. per ton, sufficient to dissolve 5.7 oz. gold or 3.1 oz. metallic silver.

In working with deep tanks, and especially at high altitudes, it is important to remember that the solubility of oxygen varies with the absolute pressure (gauge + atmosphere). In a slime tank containing pulp of specific gravity P , at a depth of H ft. from the surface, the gauge pressure (pounds above atmosphere) = $0.433PH$. Thus in a Pachuca tank, 45 ft. deep, filled with pulp of specific gravity 1.2, the pressure at bottom = $0.433 \times 45 \times 1.2 = 23.4$ lb. per sq. in.

If this is at an elevation of 5000 ft., with barometer standing at 25 in. ($25 \times 0.49 = 12.25$ lb.), the solubility of oxygen at the bottom will be nearly treble that at the surface.

$$\frac{23.4 + 12.25}{12.25} = 2.91$$

In working with thick slime the rate of solution of oxygen, like that of other substances such as gold or cyanide, is much diminished as compared with thin pulp or clear solution.

Solutions recently precipitated with zinc or aluminum, especially after vacuum treatment, are practically free from oxygen and nearly saturated with hydrogen and, therefore, in the most unfavorable condition for dissolving gold; they should be given an opportunity to aerate by cascading, spraying, or agitation.

Heating Solutions.—Both the dissolution and precipitation of precious metal, as well as the settling of slime, are accelerated by a moderate rise in temperature, and systematic heating of solutions has often been proposed. It has been advantageously carried out with extremely cold solutions, or to assist in thawing frozen ore. Heating above 50 or 60°F. is, however, of doubtful value, as it diminishes the solubility of oxygen and favors decomposition of cyanide.

When exhaust or cheap steam is available, it may be led through coils or zigzag pipes near the bottom of solution tanks or sumps; conveying pipes and launders should also be protected from cold.

The settling of slime and filtering of solution through sand are also facilitated by heating; the rate of settling (and, therefore, the capacity of settling tanks, etc.) is inversely proportionate to viscosity of liquid. The settling rate of a slime is proportional to $T + 10$, where T = temperature Fahrenheit. Thus if a particular slime settles 18 in. per hr. at 40°F., its settling rate at 60° will be $\frac{60 + 10}{40 + 10} \times 18 = 25.2$ in. per hour. The same rule holds approximately for filtration rates.

In crushing ore, most of the energy applied to the machines becomes available as heat in the resulting pulp. As the specific heat of most ore and rock is between 0.2 and 0.25, that of solution being practically 1, it is easy to compute roughly the rise of temperature that may be expected. With low water ratios it is often of importance as an insurance against freezing. One hp.-hr. = about 2550 B.t.u. and raises a ton of water about 1.25°F., or a ton of dry ore 5 to 6°F.

Fouling of Solutions.—In the earlier days of cyaniding much was said of the fouling of solutions, and it was necessary at times to dispose of "fouled" solution and make a fresh start. This is now rarely necessary; solutions are used continuously for many years without renewal and without material change in composition. The daily elimination of solution in residues, and in first and last drainings, is an appreciable percentage of the whole stock of plant solution, so that the solution is practically renewed every few months.¹ Zinc is removed to some extent by precipitation or adsorption on the ore or tailing.

Regeneration of the cyanide usually lost as a solvent has proved an attractive field for invention, but so far has met with comparatively little success. The following lines have naturally suggested themselves.

1. Precipitation of precious metal by a metal simultaneously regenerating NaCN, such as Na directly, or Al indirectly; Zn itself has some effect, as its double cyanide is a feeble solvent, rendered more active by the presence of free alkali. Electrolytic precipitation may be included here.

2. Oxidation of HCNS to HCN + SO₂ or of NaCNS to yield NaCN + SO₂, the latter with alkali forming sulphate. This may be effected by electrolysis or by certain oxidizing agents, but the yield has always been disappointing, owing to decomposition of the product. In this connection, reference must be made to the Clancy project.

3. Neutralization or acidification of solutions; on the one hand, yielding insoluble cyanides [CuCN, AgCN, Zn(CN)₂; CuCNS, AgCNS; occasionally ferrocyanides], and on the other, liberating HCN. The precipitates must be separated to recover Au, Ag, and part of their contained CN by suitable means; the HCN may be removed at least partially from the solution by heat, by passing a current of air or gas, or by applying a vacuum as in the Crowe process. Gaseous HCN thus liberated may be absorbed in a suitable alkaline solution to form NaCN or Ca(CN)₂, or the HCN in solution may be fixed by addition of alkali.

The general idea has been to operate upon "fouled solutions" or on the "low solution" normally and unavoidably thrown away daily in some form. The low

¹ If p is the percentage of stock solution discharged daily, and x the percentage of any substance now present remaining in the system after n days,

$$\log x = n \log \left(1 - \frac{p}{100} \right) + 2$$

Thus, supposing 5 per cent of the stock is daily removed, only about 21.51 per cent of any material now in solution will remain after 30 days, 4.6 per cent after 60 days, less than 1 per cent after 90 days, etc. Hence, if any radical change is made in the treatment, such as substituting NaCN for KCN, the solutions soon reach practical equilibrium.

concentration of solutions in general use has militated against the completeness of precipitation and volatilization.

Filter Cloth.—Many varieties of filter cloth have been used in cyaniding ore, precipitation with zinc dust, and handling acid-treatment liquors. Cotton cloths of all the three common weaves—plain canvas with single or double thread, twill, and sateen—have been found satisfactory when the weight of material selected is suitable for the pressure and conditions of use. The more complicated weave known as chain cloth seems to have no sufficient superiority to justify its price. Paper is not generally to be recommended.

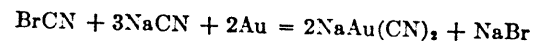
For precipitation it is convenient to use one of two systems: (1) a fairly heavy cloth backing, covered with light "domestic" or twill, the latter to be removed at each cleanup and burned, or washed and re-used once or twice; or (2) two layers of a medium-weight material, the outer to be removed at cleanup and either burned or washed for re-use. When re-clothing, a new or washed cloth is put next the plate and the original under cloth replaced above it. Occasionally three or four thicknesses of very light material have been used, the outer layer being taken off at cleanup and a new one placed next the plate.

For filter bottoms of leaching vats a heavy canvas (such as No. 8 or 10-oz. duck) is desirable and will last one to two years. It may be acid-treated in place if the usual accumulation of calcium carbonate checks the leaching rate decidedly. A similar cloth may be used in filters of the Moore and Butters types; for slime presses a similar heavy canvas may be covered with a light or medium twill. These may similarly be acid-treated by using hydrochloric acid, so highly diluted as to avoid attacking the iron frames.

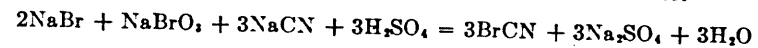
The nominal "ounces" rating of canvas refers to the weight of a running yard of a standard width of 22 in.; the "ounces" may be read directly by noting the weight in grams of a sample cut 4 × 7 in. (28 sq. in., or 180 sq. cm.). The "number" is approximately obtained by subtracting the "ounces" from 19. Thus if a sample of duck, 4 × 7 in., weighs 9 g., it indicates "9-oz." duck, or "No. 10." Figures thus determined usually agree within one unit with the commercial ratings, but dealers occasionally apply the ounce rating to the square yard, making the nominal weight about 60 per cent too high. The present tendency is to specify weight per square yard, irrespective of the actual width of fabric.

MODIFICATIONS OF THE CYANIDE PROCESS

Bromocyanide Process.—This depends on the reaction



the BrCN being added as such, or obtained from bromide and bromate:



The bromocyanide process has been used in Western Australia, and to a limited extent in Canada and Colorado. An excellent résumé with bibliography is given by Stevens and Blackett.¹ Bromocyanide can be used to advantage only on two classes of ore: (1) ores containing minerals such as tellurides, more soluble with this reagent than with plain cyanide; (2) ores requiring rapid dissolution of gold in order that other substances in the ore shall not have time to dissolve and foul the solution. A preliminary treatment with plain cyanide is always advisable. No appreciable amount of free alkali must be present. BrCN itself decomposes rather rapidly in solution and also induces wastage of NaCN. BrCN is rather

¹ Trans. I.M.M., Vol. 29, p. 280.

expensive, and so are the mixtures from which it may be prepared (Br + NaOH + NaCN, or NaBr + NaBrO₃ + NaCN), and the "mixed salts" used for this purpose are liable to decomposition in storage. Cyanogen chloride cannot be substituted, and ICN is too expensive.

Gitsham Process.—Free HCN in the presence of oxygen has a slight solvent action on gold. This process proposes to use feebly acid solutions, especially for ores containing antimony, copper, and other base metals. The effluent solutions are to be neutralized by lime before precipitation by zinc, and reacidified with addition of enough alkaline cyanide to bring them up to suitable strength.

Gilmour-Young Process.—This system was devised at a Kicaragua mine to utilize the existing Boss process pans for cyaniding rich ore. Copper amalgam was made by treating mercury with copper sulphate and iron filings, the squeezed product carrying about 15 per cent copper; zinc amalgam was sometimes added. A charge of dry ore was ground with cyanide solution and about 200 lb. of mercury for 2 hr.; 30 lb. of copper amalgam was then added, and the whole ground 4 hr. longer, when the mercury was separated. The squeezed amalgam was enriched by repeated use and finally retorted, yielding bullion 700 to 750 fine.

Diehl and Marriner Processes.—These were evolved to treat the rich telluride ores of Western Australia. The Diehl process consists in wet crushing, sliming, and treatment first with KCN and then with BrCN in agitation vats and filter presses. The Marriner system involves dry crushing, roasting, amalgamation, and treatment of the roasted ore by percolation or by fine grinding and filter press. There were many modifications of each system in use; the results and costs did not differ greatly, as the cost of bromocyanide in one case offset that of roasting in the other. With the wet process, concentration was often practiced, and the concentrate roasted preparatory to cyaniding.

The Usher process was an African slime method in which, after one stage of agitation, solution was introduced by multiple pipes over the bottom of a flat or cone-bottomed tank, and the upper clear portion continuously decanted for precipitation. Finally the slime was allowed to settle as usual. In one modification of the process umber, containing manganese peroxide, was used as an oxidizer.

The Denny desulphurizing process is used at the Nipissing Mine, Cobalt, to prepare silver sulphide ores for cyanidation. By grinding them in tube mills with ingots or slugs of aluminum and caustic soda, all silver minerals are decomposed, except dyscrasite, yielding metallic silver which is amenable to cyanide. At the same time Na₂S is formed, which can be used as a precipitant. The process is completed by agitating the pulp 12 hr. in a tank lined with aluminum plates.

Antidotes to Cyanide Poisoning.—The following materials should be kept at every cyanide plant and laboratory; sets should be placed at convenient points on every floor at which solutions are handled.

One sealed bottle (preferably a quick-opening "citrate of magnesia" bottle with rubber gasket), containing 1.5 g. of caustic soda, NaOH, dissolved in 300 cc. of water.

One sealed bottle (preferably a 2-oz. wide-mouthed bottle with large projecting cork), containing 7.5 g. (¼ oz.) of ferrous sulphate crystals dissolved in 30 cc. (1 oz.) of water. This water should be freshly boiled, and the vacant space in the bottle filled with carbon dioxide or hydrogen, to prevent oxidation; the cork must be completely covered with melted paraffin or sealing wax.

One corked tube containing 2 g. of finely powdered magnesia.

A large cup, of at least a pint capacity, preferably of white enamelware, which will hold the three previous items, together with a spoon or flat stick for stirring them. When required, the ferrous sulphate is to be poured into the cup, followed by the soda and magnesia, and the whole well stirred and swallowed; no time should be wasted.

It is desirable to add a rubber stomach tube and a wooden gag, so that the antidote may be poured into the stomach of an unconscious patient if necessary.

These materials should be kept in a glass-fronted cupboard, easily accessible and conspicuously marked, and all foremen and shift bosses fully instructed in their use. The soda requires renewal after 2 or 3 years, as it slowly attacks glass. The ferrous sulphate also oxidizes slowly, but a small amount of yellow deposit may be ignored, as long as the solution remains strongly green.

The above is known as the Martin antidote, and was developed by Dr. C. J. Martin and R. A. O'Brien, of Melbourne, in 1902. Variations of the outfit have been put on the market by different dealers, but the equipment can be easily prepared at any laboratory. The essential reaction is the formation of ferrous hydroxide, avoiding any excess of caustic soda, and conversion of the cyanide into harmless ferrocyanide.

Among other remedies that have been suggested are: hydrogen peroxide (2 per cent solution used hypodermically and as a stomach wash), cobalt salts, adrenalin, sodium cacodylate, and silver nitrate (dilute solution followed by an emetic of salt water and mustard).

Safety Plant Precautions.—An eczematous condition of the skin may be caused by long contact with strong cyanide solutions. This should be avoided at cleanups of zinc boxes by greasing the hands and wearing rubber gloves in handling wet shavings; it is unnecessary to handle solution at other times.

Zinc shaving and dust, and aluminum dust, are decidedly inflammable. Caustic soda falling on zinc dust reacts with the evolution of enough heat to ignite the liberated hydrogen and cause the zinc to smoulder. Extinguishers of the carbon tetrachloride type must not be used on zinc-dust fires, as the reaction ($Zn + CCl_4$) yields various toxic and irritating gases.

MINOR AND OBSOLETE PROCESSES

Chlorination Process for Gold.—This process was based on the fact that chlorine, in the presence of moisture, converts gold into the trichloride ($AuCl_3$), which is soluble in water and removed by washing; the gold being then precipitated by ferrous sulphate, sulphur dioxide, hydrogen sulphide, or charcoal. Coarse gold requires long contact and should be removed by amalgamation. Pyritic ore or concentrate requires a dead roast before chlorination; thoroughly oxidized ore may be treated directly. Basic ores—containing lime and especially magnesia—absorbed much chlorine and might become heated. This was checked by roasting with a high temperature at the finish, to frit the magnesia with silica. Chlorination was suggested by Percy and by Plattner independently in 1848, though Plattner apparently made the first commercial application of the process to the arsenical ores of Reichenstein, Silesia.

The *Deetken* or *California* process was carried out in comparatively small wooden vats with bottom filter of perforated boards, resting on slats and covered with coarse gravel and sand; a vat 8 ft. in diameter with 3-ft. staves would hold about 3 tons. The crushed and roasted ore was loosely charged by sifting in a moist condition to facilitate leaching, a cover was luted on with clay or dough, and gaseous chlorine generated in a lead vessel from manganese dioxide, salt, and sulphuric acid was admitted by a lead pipe to the bottom until it could be detected at a hole in the cover. In later practice, liquid chlorine was purchased in steel cylinders. After 12 to 36 hr. contact (adding more chlorine if necessary), water was turned in at the top, any chlorine escaping at the bottom pipe being led to another vat. The yellow solution was run to the precipitating vat and the charge washed until the effluent was colorless. The residue was then shoveled out; if much silver was present it was transferred to another vat

and leached there with hyposulphite solution. Some ores, rich in silver, were first leached with hyposulphite and then chlorinated.

The *barrel* process, used on a large scale in Colorado, involved the rotation of the ore in barrels of wood or heavy lead-lined steel, holding 5 to 25 tons, while chlorine was generated under pressure in the mass by means of bleaching powder and sulphuric acid. Barrels were often built with an internal filter on one side, consisting of pebbles or coarse sand confined by slotted boards and a perforated lead plate. After 3 to 6 hr. water under 20 to 40 lb. pressure was admitted by a trunnion and washed the charge in 1 to 2 hr. A ton of ore would use at least 10 lb. of bleach and 15 lb. of sulphuric acid. The ore was charged dry from a hopper and discharged by sluicing through manholes in the side.

The *Munktell* process consists in leaching the ore with two solutions, one of bleaching powder, the other sulphuric acid, which mix at the time they are applied. At Mt. Morgan, Queensland, a solution of chlorine in water was similarly used, 100-ton charges of ore being leached in rectangular concrete vats, $60 \times 12 \times 5$ ft., lined with pitch and provided with bottom filters of sand resting on perforated planks and joists. This was superseded by the permanganate-chlorine process.

The *Black-Etard*, or permanganate, process employs long contact with a solution of potassium permanganate, salt, and sulphuric acid (about 6 lb., 120 lb., and 140 lb. to 5 tons or 1000 imp. gal. of water), the color indicating its strength. The original Etard formula used permanganate and hydrochloric acid.

The *Mears* process is barrel chlorination in which gaseous chlorine is pumped into the charge under its own pressure. Thies first employed bleaching powder and acid to produce the pressure. Newbery and Vautin used air pressure to accelerate the action of the chlorine, and the Pollok patents specify water pressure. Ankeny used the more expensive bromine in place of, or in conjunction with, chlorine. Many other early patents dealing with chlorine and bromine are described in O'Driscoll's "Notes on the Treatment of Gold Ores."

In California, precipitation was usually effected by ferrous sulphate, made by the action of sulphuric acid on scrap iron. Sulphur dioxide was commonly used in conjunction with the Colorado barrel process, generated in iron retorts from sulphuric acid and sulphur or charcoal, or hydrogen sulphide, and sawdust filters. Charcoal was used as precipitant at Mt. Morgan. The solutions were usually passed through boxes filled with scrap iron to precipitate copper or silver before being discharged.

Roasting was usually effected in California by hand-rabbed wood-fired reverberatories; elsewhere in White-Howell or Bruckner cylinders, Pierce turret furnaces, Merton or Edwards furnaces, etc. At Mt. Morgan the Richards furnace was used, cascading the ore from successive shelves. Residues from pyritic ores were often ground for paint.

The *Patera* process utilizes the solubility of silver chloride in solution of sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$ (the hyposulphite of photography) and precipitation of silver as Ag_2S by Na_2S . This was suggested by Percy and first applied by von Patera at Joachimsthal in 1858.

The ore is roasted with addition of salt (4 to 8 per cent), part of it being added near the finish; the hot ore is wetted and allowed to stand some hours to favor chloridizing of the silver. It is then bleached in wood vats with warm water to remove base-metal chlorides which also dissolve a little $AgCl$. Hyposulphite solution is then applied and finally wash water, and the effluent run to "base metal" tanks until a trace of hypo is found, then to the silver tanks. The base solution may be precipitated by Na_2S , or Ag may be thrown down by cement copper, and copper by scrap iron, or iron may be used at once. The silver solution is precipitated by sodium

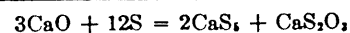
sulphide, carefully avoiding an excess; after separating Ag_2S by settling or filtration, the solution can be used again.

A suitable solvent is 0.5 per cent of crystallized $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, but up to 2 per cent may be used in absence of base metals; 1 ton of 0.5 per cent solution dissolves 30 to 40 oz. of silver. It also dissolves PbSO_4 and PbCl_2 ; adding Na_2CO_3 then precipitates PbCO_3 . Sulphates retard solution of silver; free alkali is more prejudicial.

Commercial sodium monosulphide may be used as precipitant, or a polysulphide (Na_2S_4 or Na_2S_5) may be made by heating caustic soda with sulphur (see under Kiss Process).

The vats used were generally small, occasionally up to 25 or 50 tons capacity. The precipitated sulphide was usually filtered in conical canvas bags hung on iron rings in a frame; a filter press was sometimes used. The dried precipitate was sometimes refined by charging upon fused lead on a cupel, or might be smelted with lead ores.

The Kiss process nominally substitutes calcium thiosulphate and sulphide for the sodium salts used by von Patera. The precipitant is usually made by boiling lime and sulphur by means of steam, yielding polysulphide and thiosulphate:



The precipitated Ag_2S is therefore mixed with excess sulphur, and thiosulphate is added to the solution. Starting originally with $\text{Na}_2\text{S}_2\text{O}_3$, this would gradually be replaced by the calcium salt, but part of the calcium is usually precipitated by sulphates as CaSO_4 , and additional sodium is introduced from salt in the charges. About 3 lb. of lime and 2 lb. of sulphur with a ton of water would make enough precipitant for 50 to 100 lb. of silver.

O. Hofmann states that, with ores containing little or no Cu, the percentage of silver chloridized may be increased by using CuCl_2 (or a mixture of 3 to 4 lb. bluestone and 6 to 8 lb. salt per ton of ore), added by degrees to the preliminary wash water.

In the Russell process, it is claimed that a treatment with "extra solution" containing some $\text{Cu}_2\text{S}_2\text{O}_7$ (prepared by adding bluestone to thiosulphate) extracted additional silver and was much more effective in dissolving gold.

The Augustin process consisted in giving a chloridizing roast to silver ore or matte, and leaching with a strong solution of common salt, which dissolves silver chloride to a limited extent. The silver was then precipitated by metallic copper, and the copper by scrap iron. The cement copper was then melted and granulated for re-use.

The Ziervogel Process.—Argentiferous matte was roasted to form sulphates, cautiously raising the temperature to decompose those of iron, copper, etc., while silver sulphate remained unchanged, and was leached out by hot water. The process was also applicable to ore.

Silver sulphate (Hofman and Wanjukoff) begins to decompose at 917°C . and is completely reduced to metal at 923° ; copper sulphate, stable up to 653° , is completely converted into CuO at 736° ; zinc sulphate at 767° ; ferrous sulphate passes into basic ferric sulphate between 167 and 480° , while ferric sulphate begins to dissociate at 492° and is completely converted into Fe_2O_3 at 560°C . Ag_2SO_4 dissolves in 180 parts of cold or 90 of hot water, and is much more soluble in hot dilute sulphuric acid; in either case it is precipitable by copper, iron, or sulphides.

In the Claudet process, the product of a chloridizing roast of copper pyrites was leached with solution of sodium and ferric chlorides, which dissolved AgCl , CuCl_2 , and some PbCl_2 . By addition of ZnI_2 (or NaI) silver was thrown down quantitatively as AgI , together with some CuI and PbI_2 , and any gold that may have dissolved. The precipitate was separated, washed, and reduced with metallic zinc, yielding spongy silver and a solution of ZnI_2 , which was used again as precipitant.

Or, by digesting the precipitate of AgI , etc., with sodium sulphide, Ag_2S was formed and NaI regenerated as a precipitant.

Gibb's process was similar, but employed H_2S gas as a precipitant, until about 5 per cent of the Cu was precipitated, which ensured all the silver being thrown down.

SILVER AMALGAMATION

The Patio process was originated by Bartolomé de Medina about 1557, for the rich silver ores of Pachuca, and was widely used in Mexico and in South American countries. This process is described at length in Chap. XVII, Chlorine in Metallurgy.

The Patio process was worked for some time in Nevada on Comstock ore, but failed owing to climatic conditions, and this led to the adoption of the Washoe or pan-amalgamation process.

The Washoe process, or pan amalgamation, was developed at the Comstock mines, Washoe County, Nevada, the ore being stamped dry or wet, and the pulp treated in batches, usually three per pan daily. The pans differed greatly in detail, having cast-iron bottoms with wood staves or sheet-iron sides, and a central cast cone through which ran a vertical shaft carrying a muller with cast segmental shoes; similar cast-iron dies were attached to the bottom. Means for raising and lowering the muller were provided by threaded hand wheels forming lock nuts at the top of the shaft, or by carrying the step bearing of the shaft on an adjustable lever. Three curved iron wings were usually fastened to the sides or hung from the wooden cover. A steam chamber was often provided under the pan bottom.

The charge was usually 1500 to 3000 lb., but might range from 800 to 5000. A batch of pulp was run in, after thickening in a wooden tank if wet-crushed; the muller was lowered and the charge ground 1 to 3 hr., steam being admitted to the false bottom, or run directly into the pulp by a hose. Mercury was then added, at least 10 per cent the weight of the dry pulp (often 300 or 350 lb. altogether), the muller raised clear of the dies and run 3 or 4 hr. Chemicals were generally added with the mercury, usually copper sulphate and salt, sometimes sulphuric acid or metallic iron, though the iron was often derived from the wear of the pan castings.

The pulp was then thinned with water and run to a shallow separator or settler with vertical shaft carrying four arms with iron or wooden plows. Here the bulk of amalgam and mercury separated and were drawn off at a siphon tap. In some cases this stage was carried out in the grinding pan, revolving the muller slowly.

The pulp then ran to an agitator—a deeper pan with wood sides, with four revolving arms carrying vertical slats—to settle a little additional amalgam and coarse material, and was finally drawn off, running to waste or to a settling dam. All settlers, etc., were provided with holes in the sides closed by wood plugs for discharging pulp. At the Comstock, 70 to 85 per cent is said to have been extracted from the sulphide ore, but at custom mills the usual return was only 65 per cent of the assay value of samples taken at the mortar lip.

Barrel amalgamation (Freiberg process) was carried out in stout wooden barrels rotating on a horizontal axis. The ore was roasted with salt and charged in the barrel with water and scrap iron, which dissolved silver chloride and reduced it to metal, cupric and ferric salts being also reduced to cuprous and ferrous; mercury was then added and rotation continued 16 to 20 hr., more water was then added to thin the pulp, and after a short period of rotation the mercury was drawn off and the ore washed out by a stream of water. This process was used for some time on the Comstock lode.

The cazo process or hot pan amalgamation was devised by Alonzo Barba in Peru about 1609 for rich oxidized silver ore. The cazo, or pan, first used was a small copper

pan; the later *fondon* had a copper bottom about 6 ft. in diameter and 6 to 8 in. thick, to which wood staves were fitted. Two large copper mullers were made to revolve around it, and a fire was maintained under the bottom. See pages 525 and 526 for a complete description.

The *Boss continuous process* was an attempt to make the Washoe pan-amalgamation process continuous, by using a series of steam-jacketed pans set on a slight grade so that pulp flowed from one to the other and finally through settlers; the mercury similarly flowed through a pipe system to a safe (as was done at some of the Washoe plants) where it passed through a conical canvas filter to separate solid amalgam, the filtered mercury being pumped back to the topmost pan.

The *Reese River process*, applied by Stetefeldt to the very base sulpharsenical ores of central Nevada, involved a chloridizing roast of the ore, wetting and cooling it on a floor, followed by a pan treatment similar to the Washoe process. A very impure bullion resulted. A similar system was used in Butte and elsewhere in Montana.

The *Combination process*, adopted by the Montana Co. about 1890, consisted in concentrating the gold-silver ore coming from the stamp mill before thickening the tailing and treating it by the pan process. A great economy in mercury was effected by thus removing arsenical copper minerals. The original equipment was 50 stamps with amalgamating plates, 20 frues, 24 pans, 12 settlers, 5 agitators, and finally 20 frues for the pan tailing, which was then impounded.

The *Kroehnke process* consisted in treating crushed ore in rotating wooden barrels of the Freiberg type, with mercury and a strong solution of cuprous chloride in brine, and then adding zinc amalgam; lead amalgam was used with poorer ore. The impure coppery amalgam was then purified by treatment with hot brine and bluestone acidified with sulphuric acid, and finally centrifuged and retorted. The process is thoroughly described by Schnäbel.

Conversion Tables for Assay Valuations.—In English-speaking countries the weights of precious metals are usually expressed in troy ounces (of 480 gr.) and fractions of ounces are stated in decimals, the troy pound, pennyweight, etc., being but little used. Other nations generally use the metric system for these as for other metals, and this system is adopted in many United States statistical reports. The purity or "fineness" of these metals is expressed either in carats (twenty-fourths) or in parts per thousand (millièmes), pure gold being designated as 24 k. or 1000 fine.

Gold.—The exact value of 1 troy oz. of pure gold was \$20.671834625323+, corresponding to the coinage of \$8000 from 387 oz. of fine gold, or 430 oz. of gold 900 fine, as the United States standard from 1834 to 1934. It is now \$35.00 per ounce. Standard British coinage gold is 22 k. or 916.666 fine, and the price of gold in London is 168 shillings per ounce.

Silver.—In the United States the price of silver is stated in cents per troy ounce of metal nominally 1000 fine. London quotations are pence per troy ounce of "sterling silver" 925 fine, which, except for short periods, was the standard for British silver coin from 1066 to 1920. Since 1920, British silver coins have been reduced to a fineness of 500.

1 penny per ounce 925 fine = 2.19 cents per fine ounce.
1 cent per fine ounce = 0.457 pence per ounce 925 fine.

United States silver coin is 900 fine, 110 standard oz. or 99 fine oz., coining \$128; the Mints report the fineness of silver bullion to the nearest one-half part per 1000.

The following foreign or obsolete units sometimes occur in reports: South America: 1 marco per cajon varies between 100 and 70 parts per million, or grams per metric ton. Russia: 1 dola (1/6 zolotnik) per 100 poods = 2.71 parts per million.

Nevada

FINENESS OF BULLION AND ALLOYS OF PRECIOUS METALS

Denomination	Equivalent in millimes or parts per 1,000	
1 k.....	41.666	{ 24 k. = 1 lb. troy (England) 24 k. = 1 mark (Germany, etc.)
1 grain per marc....	0.217	4,608 gr. = 1 marc of 8 oz. (France, Spain, etc.)
1 oz. per marc.....	125.000	8 oz. = 1 marc (France, Spain, etc.)
1 loth (silver).....	62.500	16 loth = 1 mark (Germany, etc.)

CONVERSION TABLES—WEIGHTS

	Grains	Penny-weights	Troy ounces	Avoirdupois ounces	Avoirdupois pounds	Grams
1 grain.....	1	0.041666	0.0020833	0.00228571	0.000142857	0.0648
1 pennyweight.....	480	1	0.0500	0.0548571	0.00342857	1.5552
1 troy oz.....	480	20	1	1.0971428	0.0685714	31.104
1 avoirdupois oz.....	437.50	18.22917	0.911458	1	0.06250	28.35
1 avoirdupois lb.....	7,000	291.666	14.58333	16	1	453.60
1 mg.....	0.015432	0.000643	0.00003215	0.000035274	0.000022046	0.0010
1 gram.....	15.432	0.643	0.03215	0.035274	0.0022046	1
1 kg.....	15,432	643	3.215	35.274	2.2046	1,000

VOLUME AND WEIGHT OF FINE GOLD AND SILVER

	1 cc.	1 cu. in.	1 cu. ft.
Fine silver:			
Weight: grams.....	10.57	173.21	299,307
Weight: troy ounces.....	0.339825	5.5687	9,622.72
Fine gold:			
Weight: grams.....	19.3	316.269	546,513
Weight: troy ounces.....	0.6205	10.1680	17,570.39

TABLE 1.—PULP FORMULAS

- d* = density or specific gravity of dry solid (ore, sand, or slime).
- p* = specific gravity of pulp (mixture of water and ore, etc.).
- S* = percentage by weight of dry solid in pulp.
- = grams in 100 g., tons in 100 tons weight, etc.
- R* = water ratio or dilution of pulp.
- = tons water per ton of dry solid.
- = grams water per gram of solid.
- V* = volume percentage of solid in pulp.
- = cubic centimeters in 100 cc. pulp
- = cubic feet in 100 cu. ft. pulp.
- F* = solid factor.
- = grams solid in 100 cc. of pulp.

= tons solid in 100 fluid tons or 3200 cu. ft. of pulp.

= avoirdupois ounces in 0.1 cu. ft. of pulp.

k is a constant for any particular solid under consideration, used to facilitate calculation, and depending upon the density of the dry solid.

$$k = \frac{100d}{d-1}$$

$$d = \frac{p}{1 - R(p-1)} = \frac{Sp}{Sp - 100(p-1)}$$

$$p = \frac{R+1}{R + \frac{1}{d}} = \frac{100}{100 - \frac{S(d-1)}{d}} = \frac{k}{k-S}$$

$$S = \frac{100}{R+1} = \frac{100d(p-1)}{p(d-1)} = \frac{k(p-1)}{p}$$

$$R = \frac{d-p}{d(p-1)} = \frac{1 - \frac{p}{d}}{p-1} = \frac{100-S}{S}$$

$$= \frac{100}{S} - 1 = \frac{100p}{k(p-1)} - 1$$

$$F = Sp = \frac{100p}{R+1} = \frac{100d(p-1)}{d-1} = k(p-1)$$

$$V = \frac{F}{d} = \frac{Sp}{d} = \frac{100(p-1)}{d-1} = (k-100)(p-1)$$

Volume percentage of water in pulp = $100 - V = 100 - \frac{F}{d} = p(100 - S)$

$$= \frac{100(d-p)}{d-1}$$

Tons of dry solid per 100 tons water = $\frac{100}{R} = \frac{100S}{100-S} = \frac{100d(p-1)}{d-p}$

Fluid tons pulp to yield one ton solid = $\frac{100}{F} = \frac{100}{k(p-1)} = \frac{R+1}{p}$

These formulas are strictly applicable only to mixtures of solids with liquids of specific gravity 1.00, such as water or cyanide solutions at ordinary temperatures.

Measurements of Daily Tonnage.—Several accurate methods are available; one depends on the direct weighing of the dried material caught during a measured interval of time; another on the measurement of time and the corresponding volume of pulp, together with the specific gravity of the pulp, using the known relations between the gravity and solid contents of pulp. Or one may estimate the flow of pulp by a weir or any other method and then determine the weight of solid in a measured volume. Reduced to the simplest terms, the computations from such data may be made by one or the other of the following formulas:

Tons solid per day = $\frac{\text{pounds dry solid caught} \times 43.2}{\text{seconds observed}} = 43.2 \times \text{pounds per second}$

Tons solid per day = $\frac{2,700d}{d-1} \times \frac{p-1}{t}$

This formula may be arranged for slide-rule calculation

where *t* = seconds required to yield 1 cu. ft. pulp.

p = specific gravity of pulp.

d = specific gravity of dry solid.

k = a constant for any particular material.

WATER AND SOLIDS IN PULP

	Weight pulp	Volume pulp	Weight dry solid	Weight water	Volume water
1 ton of pulp (2,000 lb.).....	1 ton	$\frac{1}{p}$ fluid ton $\frac{32}{p}$ cu. ft.	$\frac{S}{100}$ ton $\frac{R+1}{(p-1)k}$ ton $\frac{100p}{3200}$ ton	$\frac{d-p}{p(d-1)}$ ton	$\frac{d-p}{p(d-1)}$ fluid ton $\frac{32(d-p)}{p(d-1)}$ cu. ft.
1 fluid ton of pulp (32 cu. ft., 240 U. S. gal., 200 imp. gal.).....	<i>p</i> tons	1 fluid ton 32 cu. ft.	$\frac{(p-1)k}{100}$ ton	$\frac{d-p}{d-1}$ ton	$\frac{d-p}{d-1}$ fluid ton $\frac{32(d-p)}{d-1}$ cu. ft.
1 cu. ft. of pulp (7.5 U. S. gal., 6.25 imp. gal.).....	62.5 <i>p</i> lb.	1 cu. ft. 0.03125 fluid ton	0.625(<i>p</i> - 1) <i>k</i> lb. $\frac{(p-1)k}{3200}$ ton	$\frac{92.5(d-p)}{d-1}$ lb. $\frac{d-p}{32(d-1)}$ ton	$\frac{d-p}{d-1}$ cu. ft.
1 ton of dry solid (2,000 lb.).....	<i>R</i> + 1 tons $\frac{100p}{(p-1)k}$ ton	$\frac{100}{(p-1)k}$ fluid ton $\frac{3200}{(p-1)k}$ cu. ft.	1 ton	$\frac{R \text{ tons}}{\left(\frac{100}{S} - 1\right)}$ ton $\frac{R}{d(p-1)}$ ton	32 <i>R</i> cu. ft. <i>R</i> fluid tons
1 fluid ton of water (32 cu. ft., 240 U. S. gal., 200 imp. gal.).....	$\frac{p(d-1)}{d-p}$ ton	$\frac{d-1}{d-p}$ fluid ton	$\frac{1}{R}$ ton $\frac{d(p-1)}{100-S}$ ton	1 ton	1 fluid ton 32 cu. ft.

1 U. S. gal. of pulp = $\frac{(p-1)k}{12}$ lb. dry solid. 1 imp. gal. of pulp = $\frac{(p-1)k}{10}$ lb. dry solid.
 Metric Values.—The relation between the metric ton (of 1,000 kg.) and the cubic meter (1,000 liters) is identical with that existing between the ton of 2,000 lb. and the fluid ton of 32 cu. ft. For instance, 1 cu. m. of pulp contains 0.01(*p* - 1)*k* metric ton of dry solid. $\frac{2.6}{100d}$ 2.7 2.8 2.9 3.0
k is a constant for any value of *d*. *k* = $\frac{100d}{d-1}$
k = 106.7 162.5 158.8 155.5 152.6 150

$$\text{Tons solid per day} = \frac{(27k)(p - 1)}{t}$$

$d =$	2.5	2.6	2.7	2.8	2.9	3.0
$27k =$	4500	4390	4290	4200	4120	4050

p may be obtained by a hydrometer in the case of slime pulp, or by weighing in grams the contents of a glass or tin liter flask, or by weighing in pounds the content of a bucket graduated to hold 100 lb. of water. (Such a bucket may be 14 in. in diameter and 20 in. deep, in which case the graduation for 100 lb. is about 18 in. from the bottom.) 100 lb. water = 1.6 cu. ft. The value of t may be observed with a stop watch in filling a 100-lb. bucket, but preferably with a much larger container.

$$\text{Tons solid per day} = \frac{\text{cubic feet per day} \times \text{pounds per cubic foot}}{2000}$$

CHAPTER XII

HYDROMETALLURGY OF COPPER

BY H. A. TOBELMANN¹

Leaching is the term applied to the process of recovering a metal from an ore by a solvent or lixiviant and the removal of the resulting solution from the undissolved portion. In other words, leaching is the recovery of a metal from ore by a wet process.

In general, leaching is applied only to ores that are not adapted to treatment at an equal or greater profit by the longer-established methods, such as gravity concentration, flotation, or smelting. It has not yet been applied on a large scale to copper ores containing a considerable quantity of precious metals, as the recovery of these is not high with the usual copper lixiviants. Its most extensive application so far has been in the treatment of low-grade oxidized ore, in which the copper is largely soluble in dilute sulphuric acid.

The oxidized copper minerals, such as the carbonates and silicates, are readily attacked by a number of the more common acids and alkalies while the nonoxidized or sulphide minerals are not and must first be prepared by roasting, weathering, or other means of oxidation, either with or without added chemical agents.

The leaching of copper ores can be carried out in the following ways: leaching in place, heap leaching, and confined leaching.

Leaching in Place.²—This method is based on the fact that, when an ore body containing sulphide is broken up so that both air and water have access to the ore, the sulphide portion of the mineral is decomposed and soluble sulphates are formed. The chemical reactions involved in this transformation of sulphides into oxidized forms have been discussed by Lindgren[1]. The behavior of sulphides of the same kind may be very different, oxidation sometimes not taking place for a long period and then again taking place so rapidly as to show decomposition within a few weeks. The more porous and more absorbent the gangue, the more rapidly will the ore respond to treatment. This method, which consists of treating ore without removing it from the mine, has been applied only to exhausted ore bodies and to mines containing large quantities of ore of such low copper content as to make its removal unprofitable, and in such a broken-up condition as to be provided with ample crevices for the circulation of both air and solution.

The action is very slow, but the method is inexpensive, the principal operating cost being the pumping and distribution of the solution and the iron and precipitation expense. The efficiency of the process in any particular case cannot be determined, as there is no known method of accurately determining the tonnage and copper contents either before or after operations.

The leaching results are obtained by the intermittent circulation of water and air through the crevices in the ore. One of the greatest difficulties of the process is that the slimes gathered from the ore and the accumulated salts may in time fill these crevices and temporarily, if not permanently, protect the exposed ore from further

¹ The chapter is a major revision by the editor of H. A. Tobelmann's original monograph.

² References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

leaching action. Usually, the rate of extraction is quite rapid at first, but it decreases continually. The solutions from such an operation are nearly always impure, and precipitation of the copper by scrap iron is the only method that can be considered.

Leaching in place is neither new nor unusual and is recorded to have been successfully used on a small scale in Hungary during the fifteenth century. J. Parke Channing[2] states that copper was extracted by this process from the Eureka mine in the Ducktown district as early as 1850. According to Philip Argall[3], the Cronebane mine in Wicklow County, Ireland, was a good example of the application of this method. In this case numerous small drifts were driven immediately under the gossan, and water was introduced into the loose gossan on the surface. The solution, after being directed from one level to another through stopes and fillings, was pumped from the lowest level to the surface, where the copper was precipitated. Irving[4] refers to a similar operation at the Aznalcollar mines in Spain. It has also been applied to some of the exhausted mines at the Rio Tinto[5]. The simplicity and the effectiveness of this method remained apparently unnoticed in the United States until the spring of 1923, when the Ohio Copper Co. of Utah[6] began the leaching of a large body, estimated to contain about 38,000,000 tons at 0.3 per cent copper, of thoroughly broken copper-bearing quartzite. The shattered quartzite itself was practically inert to chemical action, while the copper minerals existing principally in the fissures of this material were readily attacked by the leach solutions. Thus, there was little danger of clogging the ore body by decomposition or alteration products, as is so apt to occur in monzonite-porphry ore bodies.

The operation consisted of carefully distributing on top of the caved ore area 1200 to 1500 gal. per min. of solution made up of about two-thirds fresh water and one-third launder tailings solution. The solution going on the ore averaged about 0.3 to 0.4 lb. of copper and 8 to 10 lb. of iron per thousand gallons. This solution percolated through the caved ore and was collected at the bottom of the shaft, where it was directed to the precipitation launders, situated on both sides of a large haulage tunnel. The solution entering the launders averaged about 15 to 20 lb. of copper and 2 to 3 lb. of iron per thousand gallons. There were two parallel launders, 32 in. by 32 in. by 1600 ft. long, in which 97 to 98 per cent of this copper was precipitated. Additional launders outside the haulage tunnel were provided to precipitate any remaining copper.

It will be noticed that iron was precipitated out of solution during its passage through the ore. This may have been due to hydrolysis or to the action of the ferric sulphate on the oxidized copper minerals in the ore, or both. Should this precipitation at any time seriously interfere with the percolation of solution, the further caving of a small quantity of ore, or acidulation of the water, would relieve this condition. It is of interest that solutions both going on and coming off the ore were practically neutral. Clean scrap was used and, due to the intelligent operation and supervision, an unusually high-grade precipitate was the result. The average precipitate produced by this company analyzed over 90 per cent copper, the impurities being those due to the entrained solution and consisting principally of iron and aluminum sulphates. The cement copper usually produced from such operations will average not over 70 per cent copper. The production of such a plant is necessarily largely dependent on the fresh water available. The Ohio Copper Co. consistently produced some 700,000 to 900,000 lb. of copper per month, or approximately 30,000 lb. per day. The total cost of operation has been published[7] as being 6 to 6½ cents per pound, f.o.b. New York, a cost that is rarely equaled. Of this amount, 50 per cent represented the pumping and precipitation costs.

Leaching of a mined-out area at Ray mines in Arizona was begun in January, 1937, using fresh water only as the lixiviant, and shredded tin scrap as the precipitant.

Precipitation should be carried on underground when conditions make it practical. The warmer the solutions, the more efficient both the leaching and the precipitation will be. Also, it is more difficult to pump solutions containing copper sulphate than those containing iron sulphate. Efficient precipitation cannot be accomplished with heavy scrap iron like car wheels, slag pots, and old rails, yet this is the practice generally tried, resulting in condemning the precipitation of copper by iron in general.

Heap Leaching.—This method of leaching is probably one of the oldest, if not the oldest, of the methods for the recovery of copper from ores. It is said to have been used as early as 1752[5] in recovering the copper from cuperiferous pyrite in Spain. This method, like the one first described, depends on the natural oxidation of the sulphide minerals by continual subjection to air and water. The chemistry of this oxidation has been much discussed, but still it is not accurately known[8].

Ores, both sulphide and mixed ore, which must be removed from the mine but which are too low grade to treat at a profit by any other method, can be treated by heap leaching. This is generally carried on as follows:

Ground with a slight slope is selected. It is cleared of any growths and is then rolled and packed with clay or slimes to make it as near waterproof as possible. Large boulders of ore are selected for building culverts and cross culverts for drainage and ventilation purposes, and the drainage is directed to a common point. The ore, without crushing or other preparation, is now carefully piled on this prepared area. In some cases, it has been found helpful to classify the material to the extent of placing the coarsest material on the bottom and the finest on the top as an aid to both the ventilation and the solution circulation. The top of the ore piles is provided with distributing trenches. Solution, consisting at first of fresh water and later of waste solution from which the copper has been precipitated, is directed over the ore pile. The wetting is so conducted that, while a certain section is being saturated with solution, other sections are permitted to heat and oxidize. In each passage of the solution through the ore, the sulphates that have formed from the oxidation of the sulphides are dissolved and washed away. The solution emerging from the bottom of the pile is directed to a sump, from which it is pumped to scrap-iron precipitation launders, where the copper is recovered as cement copper. The solution with the copper removed is pumped back to the ore for further leaching.

The method is quite simple, but the reaction is very slow. As years are required to obtain a commercial extraction, this method can be profitably applied only to very large tonnages. The principal method of recovering copper at Rio Tinto has been by a heap-leaching process. Two classes of ore are leached by this method, a pyrite and a quartz. When leaching sulphides, the fines and the coarse are treated together. The heaps are 10 to 40 ft. high. The tops are divided into squares for better solution distribution. According to De Kalb[5], at one time there were about 20,000,000 tons, occupying about 350 acres, undergoing treatment. The heaps have been placed on a gently sloping hillside having a naturally impervious floor. About 150 gal. of solution per ton of ore per year is required. About 60 per cent extraction is generally made in the first 3 years, while 7 to 9 years is required to bring this up to 80 or 85 per cent. It is also said that some of these piles have been under treatment for nearly thirty years. The pyrite itself is barely attacked and is sold for its sulphur value.

Some data are also available on operations at Sacramento Hill, Bisbee, where heaps containing over 1,800,000 tons of ore were leached. In the first 21 months, 37.28 per cent of the copper was extracted at a cost of about 5.5 cents per pound. The loss of, and absorption of, water amounted to 24¼ per cent of the total sent to the heap. The first heap (750 × 1800 ft. base) had an analysis of Cu, 0.92 per cent; SiO₂, 63.5 per cent; Al₂O₃, 11.2 per cent; CaO, 0.7 per cent; S, 6.8 per cent[51].

In leaching the old waste dumps at Tyrone, New Mexico, it was found necessary to direct the leaching water into the dumps under pressure. If this was not done there was channeling, and test pits showed unleached portions. Oxidation appeared accelerated by alternate wetting and drying. Baled factory scrap was found the most satisfactory precipitating base. About 1.30 lb. was consumed per pound of copper recovered[52].

Heap roasting followed by subsequent heap leaching has been practiced. Schnäbel speaks of a process at Rio Tinto which consisted of slowly roasting elliptical heaps of sulphides containing some 1500 tons of ore. After roasting, the pile was leached with water, whereupon the larger portion of the copper was recovered. The partially leached ore was now restacked over horizontal flues to permit of thorough ventilation and was moistened from time to time, whereby much of the remaining copper was recovered. The copper was precipitated by iron.

Confined Leaching.—By "confined leaching," the leaching of an ore in tanks or vats is meant. This may be accomplished in two ways, either by agitation or by solution circulation, depending largely on whether or not the ore must be finely ground to give a profitable extraction. This form of leaching may be divided into the following principal operations: (1) reduction to size, meaning the necessary crushing, grinding, and screening; (2) the converting of the copper mineral to an oxide or sulphate by roasting or otherwise, if it exists in a nonoxidized form; (3) dissolving the copper in the cheapest and most suitable reagent and removing the resultant solution from the undissolved portion of the ore; (4) washing the treated ore so as to recover the entrained copper solution; (5) the precipitation or removal of the copper from these pregnant solutions.

Reduction to Size.—The fineness to which an ore will have to be crushed to give a commercial extraction is largely dependent on its porosity, the size of the mineral grain, the degree of dissemination, and the rapidity with which the mineral is attacked by the lixiviant used.

In most cases where copper ores are treated by leaching, the mineral exists as seams or filling of fissures, and fine grinding is resorted to only when rapid extraction is desirable or necessary. Rarely, however, is the copper-bearing mineral so disseminated and so surrounded by an impervious gangue that fine grinding is necessary for releasing the mineral particles in order to give access to the solvent. The typical material leached at Chuquicamata is an example of the copper mineral occurring in seams and the filling of fissures, whereas the material treated at Ajo would be an example of the more distributed copper minerals.

The influence of screen size on extraction can be seen from the table on page 349. This table shows the mesh, the percentage of copper in heads and in tailings, and the extraction on material of the different mesh for the year 1920 at the New Cornelia Copper Co.'s plant at Ajo, Ariz.[10]. During this year sizing tests were made of each head and tailing sample, composited monthly and analyzed. The average for the year was then computed.

The coarser the mesh that can be leached, the less will be the crushing expenses and the more efficient the circulation. As the time required to leach an ore depends almost entirely on the solution penetration, it can be seen that the larger the particle of ore, the longer the time that will be required to dissolve the copper. The treatment of coarse material entails less expense not only as to crushing, but it is simpler to remove the dissolved copper, there is less copper entrained in the final material discarded, and less impurities will be dissolved per unit acid neutralized. Coarse grinding will permit leaching by percolation in tanks in which the material is stationary and the lixiviant moving, so that leaching and removal of the dissolved copper from the gangue are coincident.

DISTRIBUTION OF COPPER IN THE AJO HEADS AND TAILINGS
Heads, per Cent Copper

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3.....	26.6	1.37	1.23	0.14	1.28	0.09
On 4.....	18.6	1.33	1.18	0.15	1.23	0.10
On 6.....	13.2	1.39	1.25	0.14	1.30	0.09
On 8.....	9.1	1.46	1.30	0.16	1.34	0.12
On 10.....	6.4	1.55	1.39	0.16	1.43	0.12
On 14.....	5.0	1.62	1.46	0.16	1.49	0.13
On 20.....	3.1	1.75	1.57	0.18	1.62	0.13
Through 20.....	18.0	2.06	1.82	0.24	1.88	0.18
Calculated.....	100.0	1.534	1.368	0.167	1.416	0.118

Tailings, per Cent Copper

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3.....	25.8	0.47	0.35	0.12	0.37	0.10
On 4.....	20.1	0.32	0.21	0.10	0.23	0.09
On 6.....	12.5	0.25	0.14	0.11	0.15	0.10
On 8.....	8.7	0.21	0.10	0.10	0.11	0.10
On 10.....	7.2	0.21	0.09	0.12	0.10	0.11
On 14.....	4.8	0.21	0.11	0.10	0.11	0.10
On 20.....	3.8	0.22	0.11	0.11	0.12	0.10
Through 20.....	17.1	0.35	0.19	0.16	0.18	0.17
Calculated.....	0.328	0.210	0.122	0.223	0.110

Per Cent Extractions

Mesh	On total copper	On oxide copper	On sulphide copper	On soluble copper
On 3.....	65.69	71.5	14.3	71.1
On 4.....	76.00	82.2	16.5	81.3
On 6.....	82.03	88.8	21.4	88.5
On 8.....	85.62	92.3	31.3	91.8
On 10.....	86.45	92.8	25.0	93.0
On 14.....	87.04	92.4	37.4	92.6
On 20.....	87.43	93.0	38.8	92.6
Through 20.....	83.01	90.2	29.2	90.4
Calculated.....	78.50	84.9	27.0	84.3

In treating coarse material, it is very important to have as much of the material of the same mesh as is practical, as oversize will not be leached and fines will interfere with solution percolation. The necessity of a uniform product for consistent extractions resulted in the adoption of disk crushers[11] at Ajo.

As a rule, the richer the material to be leached, the finer the grinding necessary for economical extraction. However, the smaller the mesh, the greater the quantity of slimes produced and the less efficient will be leaching in tanks. Slimes, when present, cause channeling, which prevents even distribution of solution and interferes with uniform extraction. When fine grinding is resorted to, the material must be classified and the sands and slimes separately treated. Where no classification and separate treatment is feasible, the product must carry the minimum quantity of fines to prevent interference with percolation.

When finely divided material is leached, both the solids and the solution are moving and the separation is accomplished by the standard methods of settling, decanting, and filtering. Probably the coarsest material being treated by a leaching process in tanks and by circulation is at Chuquicamata, where 90 per cent of the material is crushed to pass a 0.371-in. screen. At Ajo about 27 per cent remains on the 0.261-in., or approximately $\frac{1}{4}$ -in., screen.

The importance of proper crushing may be seen by the following: If the ore leached at Ajo had been so crushed that the material remaining on 3 mesh were crushed to pass 3 mesh but not to pass 4 mesh, the extraction would have been increased a little more than 2 per cent, or approximately 0.6 lb. of copper per ton of ore.

In any form of leaching, whether with an acid or an alkali solvent, slimes must be avoided as much as possible.

Oxidation or Roasting of Sulphides.—As has already been stated, copper in an oxidized form is quite soluble, while in the sulphide form it is not. Roasting, which is essentially oxidation, is resorted to, and ores that are proposed to be treated by a wet process and that consist of all or part sulphides must be roasted.

During roasting, sulphides are not only oxidized or converted to sulphates but under proper conditions a large part of undesirable elements, like arsenic, antimony, and bismuth, can be volatilized. Heat-treatment, such as roasting or thorough dehydrating, is an advantage to many ores, making the impurities less soluble and leaching and filtration less difficult.

To obtain the best results, the proper roasting conditions must be determined for each ore. The literature on the subject is extensive and covers a great many different conditions. It has been found possible under proper conditions so to roast an ore as to convert practically the total copper present in a mixed ore to a water-soluble sulphate[12].

Roasting is frequently carried on in the presence of, or with the aid of, a reagent, usually sodium chloride, or common salt, with the object of converting the copper into a more soluble chloride and the silver into a more soluble compound. Roasting with sodium chloride, however, requires careful regulation of temperature, since, under certain conditions of temperature and certain ratios of salt and sulphur, the copper may be almost completely volatilized (see Chap. XVII, Chlorine in Metallurgy).

Dissolving the Copper.—Many lixivants have been proposed for dissolving the copper in an ore. These include both acid and alkalies and are, in order of their importance, sulphuric acid, ammonia and ammonium carbonate, ferric sulphate, sulphurous acid, ferric chloride, cupric chloride, hydrochloric acid, chlorine, and nitric acid.

Of these, sulphuric acid is the cheapest and the solvent most commonly used. It reacts readily with the oxidized copper minerals, forming copper sulphate. Its action on the copper sulphide minerals is practically negligible. It is, unfortunately,

also a ready solvent for many other constituents of ores in which the copper minerals occur—in some cases, to such an extent that it cannot be profitably used. It is always used as a dilute solution, probably never exceeding 10 per cent and seldom exceeding 5 per cent, depending upon the grade of the ore, the time of contact, and the temperature of the lixiviant. Sulphuric acid has a selective action for copper and in very dilute solution will react with copper in preference to the other constituents of the ore.

It has long been recognized that in the leaching of copper ores, as in cyaniding gold ores, the product of the time of contact and the solution concentration is a constant. In other words, if a given ore is leached on a given mesh for 8 days with an average acid concentration of, say, 2.5 per cent, the same extraction will be obtained as when leaching this material 16 days with half the acid concentration, or 1.3 per cent. The important fact, however, is that in the case of the greater concentration only 50 per cent of the acid was used in dissolving copper, while more than 75 per cent was used when using the lower acid concentration. In other words, the lower the acid concentration, the less impurities will be dissolved. In leaching with sulphuric acid, the acid is one of the largest, if not the largest, item of expense, and when electrolysis is used to precipitate the copper, much of the acid combined with elements other than copper is permanently lost. Impurities are objectionable not alone from the point of excessive acid consumption, but also because of their accumulation when the method of precipitation is such that the solution may again be used. Also, impurities may accumulate in a solution to such a point that it will be no longer efficient and it will have to be discarded. The largest leaching plants operated, Chile Copper Co. at Chuquicamata, the now abandoned New Cornelia Copper Co. plant at Ajo, Ariz., and Andes Copper, at Potrerillos, used dilute sulphuric acid as the leaching agent.

The subject of sulphuric acid leaching processes would not be complete without reference to the excellent process devised by Greenawalt[29]. While this process is very similar in many respects to that used at Ajo, each was developed independently. The Greenawalt process has two outstanding features. These are (1) the continuous reduction of the ferric sulphate with sulphur dioxide by circulating the cell solution in closed circuit with the reducing apparatus; (2) the precipitation of the copper in the discard solution by means of hydrogen sulphide instead of with scrap iron as at Ajo.

This process is applicable to oxidized as well as to roasted sulphide ores. By this continuous reduction feature, Greenawalt states that he is able to reduce the copper content of the solution going through the electrolytic cell to a greater degree than with simple reduction as carried on at Ajo.

For the removal of the copper from the solution that must be discarded, Greenawalt uses hydrogen sulphide. This is effective in various acid concentrations and has the advantage of leaving the solution in condition for further use as a lixiviant should this be desired. It is very doubtful, however, if the cost of the precipitation of the copper from waste solutions by hydrogen sulphide is less expensive than precipitation by scrap iron. From tests conducted at Ajo, the costs are about the same, while the solubility of the copper sulphide precipitate in dilute ferric sulphate is not appreciably different from that of cement copper.

The main feature of the Greenawalt process is the continual generation of sulphuric acid. The process, when operated under proper conditions, may be made self-sustaining. As the cost of sulphuric acid is one of the largest items of expense in leaching, the advantages of this process may readily be seen.

At Ajo, where the ferric sulphate in the solution going to the electrolytic cells was reduced with sulphur dioxide, there were periods when the sulphuric acid produced in the towers alone was sufficient to carry on the leaching process.

Ammonia and Ammonium Carbonate.—Next to sulphuric acid in importance and efficiency as a leaching agent may be mentioned ammonia and ammonia compounds. In the presence of air, ammonia and ammonia salts react quite energetically with metallic copper and oxidized copper compounds. The active constituent is the cupric ammonium carbonate that is formed and which reacts with the copper minerals, forming cuprous-ammonium carbonate. In the presence of air, the cuprous compound is rapidly oxidized to cupric, and again becomes an active leaching agent. When a solution containing cuprous or cupric ammonium carbonate is heated, both the ammonia and the carbonic acid are distilled off and condensed while the copper is precipitated as a cuprous or cupric oxide. There is no fouling of solution.

This process is said to have been originally developed in Germany[13, 14]. In 1871, in a paper read before the A.I.M.E., the matter of native-copper losses in the Calumet & Hecla tailings was discussed and the fact brought out that this copper could be dissolved in solutions of ammonia salts. Some years later when the treatment of these tailings was again considered, ammonia-leaching tests were conducted which resulted in the erection and operation of the present plant, in which some 8000 tons per day is treated.

The material treated at the Calumet plant is finely divided metallic copper in sands. This metallic copper is at all times covered with a thin film of oxide which is rapidly dissolved in ammonia in the presence of an ammonia salt. If the metallic copper is again subjected to the air, it will again be covered with a thin film of oxide which will dissolve. These reactions are the basis of the ammonia-leaching process.

The early difficulties of the process are said to have been the loss of the highly volatile ammonia which occurred both during the leaching and during the boiling of the solution. Benedict[13] found that this loss was not solely due to volatilization but to a larger extent to adsorption of ammonia by the ore particles. This loss increased with the strength of solution. By using only a weak solution, treating low-grade material, and driving off the adsorbed ammonia from the tailings by steam before discharging, Benedict found that these losses could be reduced to a minimum. This process when applied to the Calumet tailings gives an average extraction of about 80 per cent.

At the Kennecott Copper Corp. at Kennecott, Alaska[15, 16], copper carbonate, both azurite and malachite, occurred with chalcocite in dolomite and limestone. The ore was treated by milling, whereby most of the sulphide copper and about 60 per cent of the oxidized copper mineral are recovered.

The tailings from the milling process were screened at 20 mesh, the undersize going to tables and the oversize to Hancock jigs. The tailings from the coarse tables and jigs furnished the leaching-plant head, while the fine sand and slime-table tailings were treated by flotation.

The original lixiviant contained about 6 per cent NH_3 , but owing to the success of washing the ore with low-pressure live steam, concentrations of as high as 11 per cent were eventually successfully used. Much difficulty was at first experienced with corrosion of iron and steel evaporator equipment by ammonia vapor. Aluminum was substituted in the condensers and concrete in the storage tanks. The ammonia loss, after the introduction of the live-steam wash, was cut to 0.45 to 0.60 lb. NH_3 per ton of ore treated. Steam consumed was about 220 lb. per ton of ore, 55 per cent in the evaporators, 45 per cent in the steam wash. Multiple-effect evaporation was used.

An ammonia process known as the Perkins process[15] is said to have given excellent results on some of the low-grade ores of the Southwest. This process consists of heating the ore to be leached in a reducing atmosphere, during which all or a large

part of the copper mineral is converted into metallic copper. It is then leached with ammonia.

Ferric Sulphate.—Ferric sulphate is not only an active solvent of most oxidized copper minerals, but also quite an active solvent of free copper sulphides. Complete extraction is possible on oxides and on carbonates in comparatively short periods, while sulphides are more slowly acted upon. To overcome the resistance of double sulphides, such as chalcopyrite and bornite, to this reagent, a partial roasting was suggested by Thomas. This was found very helpful, and under proper roasting conditions commercial extraction may be obtained from sulphide ores with ferric sulphate as the lixiviant. Heat was found to promote the leaching reaction.

Much careful work has been done with this reagent. Probably the earliest is that of Siemens & Halske, who, in 1890, introduced a process that consisted of leaching an ore ground to 90 mesh with hot dilute ferric sulphate. The copper was precipitated electrolytically, using insoluble anodes and the lixiviant regenerated. The results obtained by Siemens & Halske were disappointing and did not warrant its further introduction. This work, however, is the basis of most ferric sulphate processes. There is no doubt that, had there been available to these investigators the present knowledge of the use of insoluble anodes, diaphragms, tank linings, etc., the results would have been very different.

Among the large-scale tests made with this reagent, probably the more important are those made at Cananea, Sonora, by the Cananea Consolidated Copper Co.[24] and at Ray, Ariz., by Westervelt[24]. At Cananea the principal difficulty encountered appeared to be the regeneration of the lixiviant. At Ray, the raw ore was leached with hot dilute ferric sulphate and the copper was precipitated electrolytically. This later work was practically a modification of the Siemens & Halske process, and, as at Cananea, the regeneration of the solvent appeared to be the principal difficulty.

In heap leaching, as practiced at Rio Tinto, where copper is extracted from massive iron pyrite, the extraction depends upon the action of ferric sulphate. By proper control of the ventilation and the wetting of this ore, ferrous sulphate is formed, which, on further action, changes to ferric sulphate and, as such, dissolves the copper.

Sulphur Dioxide.—Sulphur dioxide is readily absorbed by water, forming sulphurous acid. As such, it is an active solvent of many oxidized copper compounds. It can generally be cheaply and easily secured, as nearly all districts containing copper also contain some sulphur.

Ore containing high acid-soluble constituents are especially adaptable to sulphur dioxide leaching. Copper sulphite is formed. This is unstable and is readily converted into cuprocupric sulphite and copper sulphate. Cuprocupric sulphite is slightly soluble in water, but is easily soluble in sulphur dioxide and in cupric sulphate.

The use of sulphur dioxide as a leaching reagent has been very attractive, with the result that much experimenting has been done and many processes have been devised. Of these processes the earliest one is probably that of Neill and Burfiend, a patent for which was issued about June, 1902. This process consisted of subjecting the ore to the action of sulphur dioxide to dissolve the copper, removing the solution from the ore and then heating it to drive off the excess of sulphurous acid and precipitate the copper as sulphite.

The process was given a rather extensive trial on the sandstone copper ores of northwestern Arizona[18], but the work was discontinued before the value of the process was definitely established. The instability of the copper compounds appeared to be the principal difficulty. Joseph Irving, Jr.[23], describes some leaching tests made at the Nevada-Douglas Consolidated Copper Co., where wetted fine ore was brought in contact with hot sulphur dioxide gas. The copper was precipitated upon scrap iron. The process was devised by G. C. Westby and S. S. Sorenson.

Many other commercial or near commercial tests were made along similar lines, but up to this time (1942) there are no large installations of this kind either in process of construction or in operation. That this reagent has many attractive possibilities is, however, generally conceded.

This problem was taken up and seriously studied during 1917 and 1918 by the U. S. Bureau of Mines[19]. It was thought that a successful process, compact and apparently inexpensive, had been developed. The operations were simple and readily controlled. They consisted of passing a mixed ore pulp through a revolving drum containing baffles to impede the progress of the ore, countercurrent to hot sulphur dioxide gas. The copper was brought into solution during the passage of the pulp through the drum, and was later recovered either by precipitation on iron direct, or by precipitation on iron and then floating the metallic copper precipitate.

During the development of this process[20], it was found that the pulp from the treatment of a roasted cupriferous pyrite by this process contained an unexpected quantity of free sulphuric acid. Careful investigation brought out the fact that dilute sulphur dioxide gas had a tendency to oxidize the ferrous sulphate to the ferric state and produce free sulphuric acid. In other words, when ferrous sulphate is agitated under certain conditions with air and sulphur dioxide, the ferrous sulphate is oxidized to ferric and free acid is produced. It was found that the free acid concentration so produced could be carried to as high as 5 per cent.

Chlorides.—Of the various chlorides that have been suggested, ferric chloride is probably the most important, on account of its cheapness and the ease with which it may be regenerated. It not only has the property of readily dissolving the oxides of copper, but it quite actively decomposes many of the sulphides of copper. Its application as a leaching reagent for copper ores was mentioned as early as 1859.

Ferric chloride, while similar to ferric sulphate in its effect on copper ores, is less apt to form basic salts, and attacks other elements more readily. Cupric or cuprous chlorides are formed by the action of ferric chloride on copper sulphides, the ferric chloride being reduced to ferrous, and, as such, may be regenerated by chlorine.

The Doetsch process, based upon the reaction between ferric chloride and copper sulphides, was once extensively used at Rio Tinto. This process consisted of leaching large heaps of half-inch ore, previously mixed with salt and ferrous sulphate, with a dilute solution of ferric chloride. The ferrous chloride produced during the leaching was converted to ferric by bringing the solution in contact with chlorine gas, in scrubbing towers.

The Froelich process consists of agitating finely ground ore with a warm ferric chloride solution and precipitating the copper with metallic iron.

Both processes have merit and warrant further investigation.

Ferrous chloride has also been used to some extent as a leaching agent. The most notable application of this lixiviant is in the Hunt & Douglas process[25]. Roasted or oxidized ores were treated with a neutral solution of ferrous chloride and sodium sulphate. As this reagent does not dissolve arsenic, antimony, and various other elements highly objectionable to copper, the precipitate was very pure. This method was later somewhat modified, and a comparatively large tonnage of material for that time was treated by this process.

The Hoepfner process, in which cupric chloride was used as a lixiviant, at one time received much attention. The copper is precipitated electrolytically from a cuprous chloride solution; the cupric chloride which is formed during deposition, is used as the solvent for further copper. The principal obstacles to the success of this process were the tendency of the cupric chloride to dissolve the deposited copper and the necessity of continual solution purification.

Ferric Chloride

Chloridizing, roasting, and leaching have found quite wide application as the Longmaid-Henderson[35] process, which is at the present time the principal process employed in recovering copper from pyrites cinders. The crushed cinders mixed with salt and sometimes with pyrite are treated in special muffle furnaces. The material so treated is then discharged into tanks and leached with water, precipitating the copper with iron.

The advantage of chlorine as a reagent has long been recognized, and its intensive action on the ores of the various metals has been also investigated. The principal obstacles in the use of this reagent are mostly mechanical and not chemical. The application of chlorine will find its greatest field in ores carrying, besides copper, precious metal values.

Chlorine Process will yield

Nitric Acid.—The proposal to use nitric acid as a leaching agent is quite old, dating back at least to 1874. The fundamental idea is to employ the nitric acid as a catalyzer to obtain a complete oxidation of the sulphides to sulphates by means of atmospheric oxygen at a comparatively low temperature. The use of nitric acid for decomposing sulphide ores in analytical work is old. It has been proposed to feed finely crushed ore, with the proper proportion of nitric acid, into a rotating furnace, similar to a cement kiln, which is heated near the lower end to a temperature sufficient to expel completely the nitric acid and the oxides of nitrogen after the sulphating reaction is completed. The presence of sulphuric acid derived from the pyritic sulphur will assist the decomposition of any nitrates that may be formed. The sulphated ore was to be leached in the usual way. The nitric acid vapor and lower oxides of nitrogen were to be recovered by a suitable tower and scrubbing system, and converted through the agency of atmospheric oxygen and water into nitric acid. The nitric acid required is directly proportional to the quantity of sulphides in the ore.

The success of this process depends upon minimizing the loss of the nitric acid which may occur in three ways, viz., through the formation of nitrous oxide and free nitrogen, which cannot readily be converted into nitric acid; through the incomplete expulsion of nitrogen compounds from the sulphated ore; and through leakage and inefficiency of the recovery system.

The use of nitric acid as a leaching agent under certain conditions has been patented at various times. Of these, the Rankin process[21], in which ore is treated with nitric acid in a closed vessel with temperature not over 125°C., is probably the best known. This process was tried out at the Nevada Douglas Copper Co., Ludwig, Nev.[22].

From all accounts, the nitric acid process seems worthy of consideration, particularly for the treatment of low-grade sulphides as well as low-grade ore containing both oxides and sulphides.

Nitric acid is probably the most active of all solvents for copper ore and will energetically attack both the oxides and the sulphides, but the successful operation of this process will depend upon being able to obtain a high percentage recovery of this rather expensive reagent so as to distribute the cost over sufficient copper to make the process commercial.

Washing.—After the copper values have been dissolved from the ore and the solution drained off, there is still present a large quantity of dissolved copper as entrained solution. In some cases this entrained solution may amount to between one-half to one-third of the total copper dissolved from the ore. When an ore has been leached by percolation, this dissolved copper may be recovered in either of two ways: (1) by filling the interstices with water and circulating this water, draining, and repeating this operation until the entrained copper is negligible; (2) by filling the interstices of the ore with water and then drawing it off at the bottom, keeping the

material covered and the interstices filled until the draining shows a negligible quantity of copper. This latter method is called the "piston method." It is claimed to use less water, require less time, and cause less trouble than the first method. The former is the method used at Ajo, the latter is the method used at Chuquicamata.

Precipitation.—The methods of precipitating copper from the pregnant acid or neutral solutions are, in the order of their importance: (1) precipitation as the purest form of copper by electrolysis, usually from copper sulphate electrolyte; (2) precipitation as impure metallic copper by some form of metallic iron from sulphate or chloride solutions; (3) precipitation as metallic copper with sulphur dioxide under heat and pressure when applied to sulphate solutions; (4) precipitation with hydrogen sulphide as copper sulphide.

In the processes in which ammonia and ammonium carbonate are used as a lixiviant, the copper is precipitated out of solution by simply boiling off the ammonia. At the present time, the first two, only, are of commercial importance in the treatment of pregnant solutions obtained from acid lixiviants.

Precipitation by electrolysis is very similar to electrolytic copper refining. The principal difference is that in the former case insoluble anodes are used and the copper is taken out of the solution, while in the latter case the anodes are soluble and replenish the copper contents of the electrolyte as it is withdrawn.

The resulting product, electrolytic cathodes, is the purest obtainable commercial copper, is easily handled, and has only to be melted into shapes to meet commercial requirements. The impurities occurring in refinery solutions are generally more serious than those existing in leaching solutions. Refinery electrolytes are frequently apt to contain arsenic and antimony in quantities sufficient to contaminate the copper. None of the leaching solutions treated at the present time by electrolysis contain appreciable quantities of arsenic or antimony. The impurities that do occur in leaching solutions are readily eliminated by simple fusion.

Copper has been precipitated from chloride and other electrolytes, but not on a large enough scale to warrant discussion. Probably all the copper sulphate leaching solutions containing over a certain percentage of copper can be prepared for electrolysis. Its application will depend almost entirely on the cost of power.

Alumina, iron, magnesia, and sodium are the principal elements besides copper that occur in leaching-solution electrolytes. Of these impurities, the iron, on account of its alternate oxidation and reduction, thereby uselessly consuming current, is the most important one.

When electrolysis is used to precipitate copper from solution, the acid that was combined with the copper is regenerated. The impurities, however, accumulate and must be removed.

Iron Contamination Removed
This ferric sulphate problem may be remedied in three ways: (1) by the use of a diaphragm or porous partition, so that the ferrous iron that is oxidized at the anode cannot come in contact with the deposited copper at the cathode; (2) by purification of the solution previous to electrolysis; (3) by keeping the ferric sulphate contents of the electrolyte at as low a point as is possible by continual reduction with sulphur dioxide.

The use of a diaphragm anode as a method of solving the ferric sulphate problem has not been applied on a large scale, principally because no satisfactory commercial diaphragm has yet been developed. While the advantages of a properly constructed diaphragm would be very important, its use would probably be limited to cases in which ferric sulphate is to play the more important part as a leaching agent, as with the simple sulphides of copper.

Purification of solution is commercially practical. Such a method, based on the Ottokar Hoffman[26] process of purifying copper sulphate solutions and applied to the

treatment of leach solutions, was tried at Ajo. This process, invented by Pope and Hahn[27], consisted of treating the ore with two lixivants, a low and a high acid. The former dissolved much copper and few impurities, the later dissolved the balance of the copper and a greater quantity of impurities. The later solution was purified by heating, and then agitating with air after the addition of sufficient roasted copper concentrates, to precipitate the iron. The solution is filtered, the filtrate is added to the first leach liquor, and both are electrolyzed. Between 75 and 85 per cent of the total impurities in the electrolyte were removed. These tests were discontinued before the value of this process was definitely proved. *Importance*

The reduction of the ferric sulphate by sulphur dioxide is very simple and is no doubt the cheapest and most efficient way to meet this problem. Its use for such a purpose is not new, having been suggested as far back as 1908. *SO₂ Reduction*

The application of sulphur dioxide for this purpose on a large scale was quite openly ridiculed. As late as 1914, the engineers on the New Cornelia Copper Co. test plant were advised that reduction with sulphur dioxide on a commercial scale was impossible and were urged to give up this matter. No trouble was experienced except that it was found that, as may be expected, the more nearly neutral a solution is, the more easily it may be reduced. *Note Fixing Problem*

Sulphur dioxide is cheap, the application for reduction is simple, and for each pound of sulphur used in reducing ferric sulphate 3.5 lb. of free sulphuric acid is produced. About 30 to 35 tons per day of ferric sulphate is reduced to ferrous sulphate with sulphur dioxide in the reduction towers of the New Cornelia Copper Co. To obtain this result, some 35 to 40 tons of sulphide ore containing 40 per cent sulphur is roasted to a calcine containing about 6 per cent sulphur. During this operation about a hundred tons of free sulphuric acid is regenerated, or about 75 per cent of the total required by the leaching plant. Under proper conditions the acid produced by the ferric sulphate reduction will be sufficient to carry on the process without the addition of acid from other sources. *SO₂ Generator*

The sulphur contents of the gas employed in reduction is not of vital importance, although, naturally, the higher the SO₂, the more efficient will be the absorption. The gas used at Ajo was as low as 3 per cent and as high as 8 per cent, with an average of about 5½ per cent for 6 years of operation. The use of towers for reduction proved satisfactory. For the entire 6 years, the ferric sulphate contents of the solution entering the electrolytic tank house averaged 0.10 per cent or less, while for 4 years the average was less than 0.05 per cent.

Greenawalt appears to have somewhat improved the process of intermittent reduction as used at Ajo by connecting each set of depositing cells with a sulphur dioxide reducing apparatus. In this manner, the ferric sulphate is reduced nearly as fast as it forms, and the continually increasing acid contents to some extent compensate for the decreased copper contents in the resistance of the cell, and more copper can be deposited per cycle than at Ajo.

In the Greenawalt process rapidly revolving disks, the peripheries of which just touch the surface of the solution and thereby produce a continuous quantity of exceedingly fine spray, are used in place of towers for reducing purposes.

The electrolysis may be carried on in either lead-lined or asphalt tanks. The former are used at Ajo, the latter at Chuquicamata.

Lead anodes are used where the solutions contain neither chlorides nor nitrates. After 6 years of continuous operation the antimonial-lead anodes in use at Ajo showed but little loss in weight. *16 Anodes*

Carbon or graphite anodes have not been used on a commercial scale for this purpose. One pound of copper per kilowatt-hour has been the average efficiency obtained when using lead or antimonial lead anodes.

Iron Precipitation.—In solutions of low copper concentration, too high in impurities for electrodeposition, some form of iron is generally used for precipitation purposes. When metallic iron is immersed in a solution containing copper, the iron is dissolved and metallic copper is precipitated. The product of this reaction is known as "cement copper."

Metallic iron has many advantages as a precipitant: it is generally quite cheap, readily obtainable, and simple to use. Clean iron as a precipitant will, with proper operating care and conditions, produce a high-grade precipitate. The usual 30 to 60 per cent copper contents of cement copper is neither necessary nor is it good practice.

There is theoretically required 0.878 lb. of iron per pound of copper to be precipitated, provided no other iron-consuming constituent is present in the solution. Both ferric sulphate, by its reduction to ferrous sulphate, and sulphuric acid, by its action to form ferrous sulphate, consume iron when present in the solution.

Due to the impurities of the iron, consisting of the constituents of the metal other than iron and the adhering iron oxide scale which is nearly always present, as well as the iron-consuming constituents of the solution from which the copper is precipitated, the consumption of iron per pound of copper is generally about 1.5 to 2.0 lb. instead of the theoretical 0.88 lb.

For good precipitation purposes, the solutions should be of as low density as possible; they should be clear, i.e., all sand and slimes should have been settled out; the iron should be of as good grade as possible, and clean. The speed with which the reaction takes place depends, of course, upon the surface of iron exposed to solution. Pig iron acts the slowest and sponge or powdered iron the quickest. Therefore much work has been done on the development of sponge-iron process. This process would consist of reducing the iron in iron ore to metal in a finely divided state and without fusion.

The most important results were obtained at the Chino Copper Co., where a special furnace was developed for continuously producing sponge iron[39]. Here a magnetite concentrate was heated with a partly coked coal in a gastight furnace in which the charge was heated by radiation.

After the development of this furnace, the U. S. Bureau of Mines announced the development of a similar process, the reduction, however, taking place in a revolving Bruckner-type furnace, very similar to that used at Anaconda also for sponge-iron tests.

Notwithstanding the fact that much work has been done on sponge iron, there are, with the possible exception of some Second World War developments, no plants in successful and continuous commercial operation at this time.

Both heat and agitation are aids to precipitation. Fine material, such as sponge or shot iron, will permit of agitation, while precipitation with loose or baled scrap, or with pig iron, must be carried on in launders.

With a clean detinned scrap iron, the Ohio Copper Co. produced some millions of pounds of cement copper, which averaged over 90 per cent of copper. Several lots, consisting of 50 or more tons each, averaged over 95 per cent copper. These are the results obtained when using clean solution of low density and with proper supervision. The average copper contents of all the cement copper produced at Rio Tinto, where pig iron is used, is 75 per cent. At New Cornelia, where baled scrap is used, it is 60 to 65 per cent.

The chemical precipitation of copper by iron is nearly always carried on in either a sulphate or a chloride solution. In either case, it is quite necessary to reduce the ferric salts before precipitation. This may be done by passing the solution over copper or iron sulphides.

The statement frequently made that the acid must be neutralized before the copper will precipitate is not entirely correct. Precipitating copper from waste solutions on

Sponge
Fe

scrap iron is frequently done at copper refineries. These solutions sometimes contain as much as 15 per cent acid, and the copper may be entirely precipitated without complete or nearly complete neutralization of the acid.

The cement copper commercially produced contains 20 to 30 per cent water or solution. Where this material has to be transported a long distance, drying might prove economical. When drying the material, however, it oxidizes. When it is very dry, it causes trouble by dusting. Tests on drying cement copper showed, when slowly dried to 15 per cent moisture, that 60 to 70 per cent of the copper contents had been oxidized. Whether dried in air or by heat, the quantity of copper oxidized appeared about the same. Air drying is too slow to be commercial. Drying with moderate heat is probably best. The statement that cement copper in drying oxidizes so quickly as to cause spontaneous combustion could not be proved.

The disposal of this cement copper has been the cause of much discussion. Producers of this material frequently have visions of greater profits by converting this cement copper into electrolytic cathodes, casting copper, blue vitriol, or some other more profitable forms. The eventual treatment of this class of material, when in sufficient quantity, will be simple melting or fusion in a coal- or oil-fired reverberatory and, perhaps, then tapping molten copper into a refining furnace and subsequently refining so as to produce a casting copper or anodes for the electrolytic refinery. Such an operation would not require a large expenditure.

The advantages of electrolytic copper in the making of alloys and bearing metals is more and more appreciated, and the market for casting copper is irregular and fluctuating, with the result that direct uses for secondary coppers are becoming less, thus reducing the field for casting copper. In all probability, the most economical disposal of this material will be smelting and casting into anodes and shipment to a refinery.

Hydrogen Sulphide.—Hydrogen sulphide may be considered the next best precipitant for copper from leaching solutions. If hydrogen sulphide is applied to a copper sulphate or copper chloride solution, copper is precipitated as cupric sulphide and acid is regenerated equal to that combined with the copper. This regenerated acid may be used to dissolve further copper.

Hydrogen sulphide may be generated in various ways, the cheapest probably being by the action of sulphuric acid on a low-grade copper matte. Tests made with hydrogen sulphide generated from sulphuric acid and low-grade matte have given the costs of precipitation to be equivalent to iron at \$20 per ton, or about 1 cent per pound of copper.

Greenawalt recommends hydrogen sulphide for the precipitation of copper from discard solutions. There are no leaching plants known to be in operation at this time where this gas is used as the precipitant of the copper from solutions.

Sulphur Dioxide.—The most interesting process that has been developed for copper precipitation is that of George D. Van Arsdale[28], who found that, when a solution containing copper and ferrous sulphate is saturated with sulphur dioxide and is then heated under pressure, a reaction occurs resulting in the precipitation of about half of the copper as finely divided metallic copper together with the formation of free sulphuric acid. This process has been tried at several plants, and it was found that between 60 and 70 per cent of the copper could be quite economically precipitated. The principal difficulty was how to recover the remainder.

Commercial Leaching Installations.—The most important copper-leaching plants that have been constructed are briefly described below.

The Chile Copper Co.—The ore treated by the Chile Copper Co. at Chuquicamata, Chile, consists of oxidized minerals in seams and fissures affording simple and rapid extraction. The ore contains among other minerals the unusual basic copper sulphate or brochantite. The mineral is readily soluble in dilute sulphuric

acid and introduces copper sulphate into the solution, which, on electrolysis, liberates free acid. The mineral is reported frequently to be present in sufficient quantity to make the addition of acid from outside sources unnecessary.

The ore, averaging about 1.7 per cent copper, is mined with steam shovels, loaded on cars, and transported by rail to the crushers. Successive crushing operations reduce the steam-shovel size so that 30 to 90 per cent will pass 0.371-in. mesh. The plant has a capacity of over 1,400,000 tons per month.

Belt conveyers deliver the crushed ore to a traveling bridge, from which it is discharged into one of six reinforced-concrete tanks lined with asphalt, 150 ft. long by 110 ft. wide by 16½ to 18 ft. deep, set end to end and holding about 11,500 tons each. The ore is charged into one end of the tank until the top of the tank is reached, and the bridge is then advanced as such a rate as to keep the level constant. This method of charging a tank classifies the ore so that the coarsest material will be at the bottom and the finest on top.

The ore may be loaded into the tanks either into solution or into a dry vat, depending on whether or not solution is available. It is allowed to soak for 8 to 24 hr. before the first strong solution is run in. A second soaking period of 24 to 72 hr. ensues, after which a second strong solution is applied at the top. Three more strong leaches are given and then six successive washings with liquors of decreasing copper content.

A certain quantity of each solution coming from the ore is removed for the complete deposition of the copper, in order to take care of the impurities and to compensate for the introduction of wash water to the system. The impurities at Chuquicamata consist principally of the sulphates of magnesium, sodium, and potassium, together with a small quantity of nitrate and chloride. The former, while not detrimental to the operation, would accumulate to such a point as to render the solution inactive. The chlorides and nitrates go into solution with the copper and must be eliminated as far as possible. The chlorides are removed by agitating the pregnant solution in the presence of metallic copper, whereby the chlorine will be precipitated as a more or less insoluble cuprous chloride. About 85 per cent of the chlorine is removed in this manner, and about 1 ton of solution is dechlorinated per ton of ore treated. The nitric acid is eliminated by the use of a little sulphur dioxide, which is converted to sulphuric acid. Both chlorides and nitrates when present in appreciable quantities prevent the use of lead anodes.

The ore is ideal for leaching, the extraction obtained averaging consistently over 90 per cent. It has been said that each ton of ore contains between 20 and 30 lb. of what might be called latent acid.

The pregnant solution after dechloridizing is sent to the electrolytic tank house for precipitation^[30]. These tanks are of reinforced concrete. There are 1098 cells in operation. Lead anodes were at first tried in the experimental plant but were not found satisfactory. A German anode made of fused magnetite was then used. The war (First World War) with Germany made these difficult to obtain, and a ferro-silicon alloy was substituted. Later these were replaced by copper-silicon and antimonial lead anodes developed by the research department of this company.

Power for all operations is generated at a plant built on the coast, some 150 miles from the mines. Of the total power generated, a little over 80 per cent is used for copper deposition. About 0.85 lb. of copper is deposited per kilowatt-hour to the tank house. Refining furnaces have been provided, and the cathodes are melted and cast into commercial shapes at the plant, the product leaving Chuquicamata as the highest grade of electrolytic copper.

This process is being successfully applied to some four or five million tons per year, turning out at practically one continuous operation some 180,000,000 lb. of refined copper from an ore that could not be treated by any other known method.

New Cornelia Copper Co.—About the time that the Chuquicamata plant of the Chile Copper Co. was ready to begin operations, the details of the process to be used in treating the ores of the New Cornelia Copper Co. at Ajo, Ariz., had been practically decided upon.

The problem in Ajo differed from that in Chile in that the ore to be treated (1) was of a lower grade; (2) did not carry any latent acid compounds, such as basic copper sulphate; (3) was less readily soluble. On the other hand, the problem at Ajo was simpler. There were neither chlorides nor nitrates to contend with in the ore. Tests could be carried out on a larger scale and closer to the scene of actual operations; supplies were less expensive and more easily secured.

After a period covering nearly three and a half years and during which some 15,000 tons of ore were treated, a process was developed, the results of which could be positively foretold, and by which the deposit was successfully worked out.

The process adopted was as follows: (1) mining by steam shovels, the maximum size to be controlled by the size of a fragment that will pass the shovel dipper; (2) transportation of the ores in cars that will stand up to the rough service and discharge freely any fragments that passed through the dipper of the steam shovel; (3) the delivery of the ore, without any storage other than cars, directly into a crusher that will receive any fragment discharged by the car; (4) crushing of steam-shovel size to as near ¼ in. as practicable; (5) leaching the crushed ore 8 days by a countercurrent system and upward circulation, using sulphuric acid and such ferric sulphate as is inherent in the process; (6) reduction by sulphur dioxide gas of the ferric iron remaining in the neutral solutions from the leaching tanks; (7) the electrolytic deposition of part of the copper from this reduced solution, which is then returned to the leaching solution; (8) the continuous discharge of such portion of the neutral solution as is necessary to prevent accumulation of sulphates other than copper to the saturation point; (9) the recovery of the copper content of such discarded solution as cement copper precipitated on iron; (10) the treatment of a part of this cement copper with solution from the electrolytic tank house to the end that the copper be returned to the circulation and a part of ferric sulphate reduced.

Crushing.—The ore was mined by steam shovels and was loaded and delivered to the crushing plant in side-dump cars. The crushing plant was divided into two departments, coarse and fine, which were separated by a 10,000-ton storage bin.

The 10,000-ton storage bin between the coarse and fine crushers was of steel, built on an elevated reinforced-concrete platform. The ore was drawn from it automatically onto a set of five belt conveyers, equipped with magnetic head pulleys, which delivered the ore to five units of Symons vertical-shaft disk crushers. Each unit consisted of three interchangeable crushers. The first was set to crush to inch cubes. The crushed material was elevated and screened; the undersize by-passed the remaining two crushers, which were set in parallel. The oversize passed to these two crushers, which were set to crush to the desired size. The entire product was fed to a system of belt conveyers, which led through a sampling plant to the leaching vats, which furnished the only storage for the crushed ore.

Leaching.—The leaching tanks, 88 ft. square and 17 ft. 4 in. deep inside, were built of reinforced concrete with wooden bottoms. Each had a capacity of 5000 tons of crushed ore. The sides and the launders of the tanks were lined with 8-lb. lead and the bottom with 6-lb. 4 per cent antimonial lead. The filter bottom was laid over the lead bottom and consisted of 5 × 12 in. joists on edge laid on 16-in. centers, covered with 2-in. shiplap planks that were bored with ¾-in. holes on 2-in. centers countersunk from below. Under the center of the filter bottom, and at right angles to the wooden floor joists, a distributing launder was set in the floor, through which the solution enters and from which it is distributed under the filter bottom.

The lead lining on the sides of the tanks was protected from abrasion by a covering of 2-in. planks. At the top and sides of each leaching tank were two overflow launders extending the length of the tank, one end being connected with the suction of a circulating pump. The charging was done by a machine especially designed for this plant and known as the spreader bridge. It consists of a traveling bridge of structural steel which spanned the tanks and traveled, as desired, lengthwise with the row. The bridge supported a belt conveyer, which received the crushed ore from the belt on a central structure. A tripper on this belt spread the ore in the leaching tanks.

The tanks were charged by filling to the top of the tank at one side, allowing the ore to assume its natural slope, or about 45 deg., and then continuing at one side and discharging the ore at the top of the slope, allowing the coarser material to run to the bottom and the finer to remain somewhat higher up, thus giving a rough classification. The bridge is moved slowly forward as the filling of the tank progresses. This plan was suggested by the engineers of the Chile Copper Co., who have obtained the best results through this method of filling.

The crushed ore was leached for 6 to 8 days by a countercurrent system and upward percolation, using dilute sulphuric acid as the principal solvent.

The solution in each tank was circulated by two 15-in. vertical centrifugal pumps having a capacity of 3500 gal. per min. each. These were driven by direct-connected 40-hp. vertical motors. The head against which the pumps work was equivalent to the friction head of the solution passing through the ore. The discharge from one of these pumps was provided with a by-pass which permitted a portion of the solution to be advanced to the next tank. Both pumps were throttled to give a circulation of about 4000 to 5000 gal. per min. through the ore. Of this amount about 1000 gal., called the solution advance, was continuously passing through from tank to tank. The high-acid solution, which has averaged about 2.5 per cent free acid for an 8-day leach, coming from either or both the tank house and the solution storage, and going on the oldest ore, was called the "acid advance." The nearly neutral solution coming off the newest charge and going to the reduction towers was known as the "neutral advance."

Upon the entrance of a new charge into the circuit the solution remaining in the oldest tank was drained to the solution storage, where it was standardized with acid and later used as acid advance. After thorough draining, the tank was ready for the wash water.

As the copper entrained in a charge after leaching was about one-third of the total copper dissolved, the question of thorough washing was very important. Four successive wash waters with drainings were used.

The fourth wash of any one charge was used as the third wash of the succeeding charge, the third used as the second, and the second as the first. In other words, each wash water was used four times, the copper contents increasing each time, when it was incorporated into the system to make up the continuous losses of solution. These losses were due to evaporation, discard, and solution entrained in tailings.

After a charge had been washed and drained, the tailings were removed from the tank by a Hulett unloader, similar to unloaders used on the Great Lakes for unloading iron ore from boats. A heavy steel bridge on trucks spanned the leaching tanks and traveled their entire length. On this bridge traveled a trolley carrying a walking beam, bucket leg, and bucket of 12-ton capacity. The unloader had a rated capacity of 500 tons per hr. and generally excavated a tank of tailings in 10 to 11 hr.

Reduction of Iron.—In the electrodeposition of copper from a sulphuric acid solution, iron, if present, will consume electric energy, by its alternate oxidation and reduction, thereby reducing the quantity of copper deposited per unit of current. During the experimental work, the control of the ferric iron proved one of the hardest

problems to solve. A patent diaphragm anode was tried and gave good results, but was cumbersome and difficult to keep in order. Later, tests made on a process in which iron and alumina were precipitated as hydrated oxides by the addition of roasted copper ores gave good results, but the method was considered too complicated for an ore of this character. The idea was then suggested of using the natural oxides and carbonates in the ore itself as the precipitant of the ferric sulphate; in other words, the precipitation of the principal impurities in the solutions upon the charge itself. Early tests made on a small scale were very promising, but tests carried out later on a larger scale failed to give the desired results. For the first 15 or 20 days, the copper in the newest charge of ore was sufficient to precipitate all the ferric iron that was contained in the solution passing through the ore. However, as the acid concentration on each charge increased, the precipitated ferric iron was redissolved and eventually accumulated to such an extent that the iron in the solution was in excess of the copper available as a precipitant.

It was now decided to resort to SO_2 reduction. The general opinion was that this was both unsatisfactory and difficult. This proved to be the case in solutions decidedly acid, but where neutral or slightly acid solutions were used, reduction proved quite easy. For these tests elemental sulphur was used, as it was believed that a gas with the maximum percentage of SO_2 was most essential and that a rich gas could be produced only by burning elemental sulphur.

In the sulphite-pulp industry large quantities of sulphur gas are produced and absorbed, and, accordingly, the method of producing and absorbing the gas used in that industry was investigated. It was found that at some plants pyrites were used and that under proper conditions a gas of 12 per cent SO_2 could be produced. The only objection in the sulphite-pulp industry to the use of pyrites was the tendency of small calcined particles to be carried into the solution and thence into the pulp. Upon investigation it was decided to make use of the cheap and abundant supply of the high-sulphur low-copper ores of the Bisbee district.

A bucket elevator and a conveyer equipped with automatic tripper delivered the crushed ore to hoppers situated above four Wedge roasters. These roasters were 22 ft. 6 in. in diameter, had seven hearths, and were belt-driven by $7\frac{1}{2}$ -hp. motors.

The gas leaving the roasters entered a spray or cooling chamber. This chamber was 14 ft. square, 94 ft. long, and was built of 8-lb. lead supported on a wooden framework. Nozzles were distributed over the top and sides through which "neutral advance" was sprayed to cool the gas before it entered the towers. Between 90 and 100 gal. of solution per minute was required to supply these sprays. The ferric iron in the solution used in cooling the gas was practically all reduced and the solution joined that coming from the towers. The temperature of the gas in its passage through the spray chamber was reduced from 600 to 150°F. A flue connected the spray chamber with the bottom of the first pair of towers, dividing the gas equally between them.

There were six towers arranged in pairs. Two pairs of the towers were part of the original equipment and were 40 ft. high and 20 ft. in diameter. These were built of sheet lead, supported on a steel framework. The other pair were 28 ft. in diameter, 40 ft. high, and were built of ordinary redwood tank construction, hooped together with iron rods. As an additional precaution against gas leakage, the wooden towers were painted with asphalt and covered with roofing paper under the hoops. The towers rested upon a reinforced-concrete base, provided with a lead pan. All towers were filled with boards placed on edge, the width of a board apart, and in layers. Each layer was laid at right angles to the one immediately below it. The solution was distributed over the top of the towers by a system of launders provided with gas seals. Between the second and third pairs of towers was a fan which drew the gas from the

roasters through the spray chamber and a third set of towers, and forced it through the second and first sets to the atmosphere. The temperature of the escaping gas was that of the atmosphere.

The solution (or neutral advance) to be reduced traveled countercurrent to the flow of gas, *i.e.*, the most reduced solution came in contact with the strongest gas. The solution coming from the newest tank of ore was pumped to the top of the third pair of towers by a centrifugal pump. The solution distributed by launders and gas seals flowed down over the filling, thus coming into intimate contact with the rising gas. At the bottom of each pair of towers there was a concrete lead-lined sump, into which the solution flowed and was then pumped through the next pair of towers. From the first pair of towers the solution was pumped to the second pair, then to the third pair, and then to the so-called settling tank, whence it went to the tank house. The purpose of this settling tank was twofold: (1) to settle out the slime, (2) to get the benefit of the additional reduction that was found to take place in a neutral or slightly acid solution on standing.

Electrolytic Deposition.—The electrolytic tanks were housed in a structural-steel building, 166 ft. wide and 280 ft. long, having sides only partly enclosed to give good ventilation. The tanks were all on the same level, none in cascade.

The cellar, which was open on all sides, had an asphalt floor draining to gutters that led to a sump at each end of the building. There was headroom throughout the cellar to permit regular inspection of tanks, piping, and feed wires.

The electrolytic tanks were arranged in banks with aisles between. There were 12 banks of 10 tanks each and 4 banks of 8 tanks each, making a total of 152 tanks. Each tank was separated from the adjacent tank by a 3-in. air space. All tanks were made of Oregon pine, lined with 7-lb. chemical lead. The inside dimensions of the tanks were 29 ft. 7 in. long, 4 ft. 9 in. wide, and 4 ft. 3 in. deep. These tanks were supported on concrete columns and were insulated by tile blocks covered with sheet-lead caps. Each tank was provided with a 4-in. clean-out plug. There were also two perforated lead diaphragms, one at each end of the tanks, to assure a uniform circulation. The inlet to each tank was fitted with a 3½-in. diaphragm valve and a 3½-in. glazed stoneware gooseneck for insulating purposes. At the outlet end there was a lead overflow pan fitted with a 4-in. tile pipe suspended in a 10-in. lead boot connected to the discharge pipe.

Each tank had 84 anodes, making a total of 12,768 in the tank house. The anodes were of lead containing 3.5 per cent antimony, of an average weight of 215 lb. They were 40 × 51 × ¼ in. thick and were suspended by two ¼ × 1¼-in. copper bars secured to the tops of the anodes. The submerged surface of all anodes was 41 × 41 in. The spacing of anodes was 4½ in. on centers. The distance from the bottom of an anode to the bottom of the tank was 8 in., while that of the cathode was 7 in. Short circuits were prevented to some extent by providing the anodes with eight chemical glazed-porcelain insulators distributed over the anode faces.

Much doubt was expressed about the life of the lead anode, and some very positive statements were made regarding their probable length of life. Continuous service failed to show appreciable oxidation, except after years of service.

There were 77 cathodes to a tank, or 9779 cathodes in the tank house, exclusive of starting-sheet blanks. The cathodes, 42 in. square, were totally submerged. They were suspended upon copper bars by loops made from starting sheets. The original starting sheets weighed about 15 to 18 lb., while the finished cathodes weighed 130 to 140 lb.

The cathodes produced varied from 99.15 to 99.85 per cent in copper content, the impurities being principally slimes, held by mechanical entanglement. The greater the density of the electrolyte, the lower was the copper content in the cathodes

and the greater the insoluble matter, iron, and alumina. The cathodes always contained more or less chlorine, varying from 0.05 to 0.35 per cent. There being no arsenic or antimony in the ore, and little in the acid, the average arsenic content of the cathodes was less than 0.0015 and the antimony less than 0.0005 per cent.

Twenty-five tanks operated on starting sheets, each tank containing 77 starting blanks, or a total of 1925 blanks. The starting blanks were of rolled 3.5 per cent antimonial lead, 53 × 43 × ¼ in., and were large enough to allow a small amount of trimming, which was done with a squaring shear. The anodes in these tanks were 3.5 per cent antimonial lead, and were 41 × 52 × ¼ in. They did not have porcelain insulators, as these tend to spot the starting sheets. The spacing of anodes in these tanks was the same as in the commercial tanks. The tank construction and other details were likewise similar.

The electrodes hung parallel to the flow of solution (or parallel to the length of the tanks) to give a free circulation of the electrolyte. Alternate bus bars extending across the tanks connected the electrodes in parallel and the tanks in series. These bus bars, placed across the tank, divided it into seven sections or cells. The intermediate bus bars were 1½ in. wide and 4 in. deep, while the end bus bars were 1 in. wide and 4 in. deep. Soldered along the top of each bus bar was a triangular piece of copper, ½ in. high, giving a point contact to the electrode bars. Small maple blocks impregnated with linseed oil insulated cathodes and anodes from opposite bus bars. These bus bars were supported on insulated iron castings, which, in turn, rested on the tank cleats. The maximum current density was 8 amp. per sq. ft. of cathode surface when operating under normal conditions. With an average current efficiency of 80 per cent, this meant a daily gain of about 10.25 lb. per cathode, or a total capacity of 120,000 lb. of electrolytic copper per day. The drop of potential between anodes and cathodes averaged close to 2.00 volts. There was a tendency for the voltage to drop during the summer owing to an increase in the temperature of the electrolyte.

The solution flow in the tank house was part of a closed circuit with the leaching and reduction plant, receiving a continuous flow of solution from them. This flow, coming always off the newest ore, then through the towers and settler, was regulated by means of weirs and varied from 800 to 1500 gal. per min., depending on operating conditions. This volume was divided among the 16 banks of tanks, those on starting sheets getting generally a little more than those on cathodes. By this arrangement each bank of tanks on cathode received between 60 and 70 gal. per min. of reduced solution. Each bank unit consisted of either eight or ten tanks, a sump, and a 9-in. vertical-type centrifugal pump having a capacity of 1600 gal. per min. Each bank had an individual circulation of 1600 gal. per min. between it and the sump, while an overflow arrangement provided for the return of such a portion of the electrolyte as was equivalent to reduced solution added.

The current efficiency depended on the quantity of ferric sulphate present, owing to the reaction between ferric sulphate and metallic copper. The ferric iron content in the solution was kept as low as possible. With the total iron not over 2 per cent, the ferric iron in the electrolyte probably did not exceed 0.5 per cent.

At the beginning of operations in the tank house, a great deal of difficulty was encountered by the dropping of cathodes in the electrolytic tanks, due principally to the corrosive action of the ferric sulphate on the loops at the solution level and on that part of the cathode covered by the ends of the loops. Corrosion at the solution line was easily remedied by raising and lowering the solution level in the electrolytic tanks, but the corrosion of the cathode sheet between the loop ends was far more difficult to overcome. Later this condition became worse with the increase in the ferric iron and higher temperature of the electrolyte. The dropping of cathodes not

spacing
of
anodes

only caused bad short circuits in the tanks, but also made it necessary, when pulling cathodes for shipment, to pull individual sheets with tongs, which made it almost impossible to handle the daily output of cathodes. Considerable damage was also done to the lead lining of the tanks, and the danger from accidents was more than usual. Numerous schemes to overcome this difficulty were suggested and tried, until it was found that, by splitting the ends of the loop and attaching them with a Morrow machine in such a manner that the portion of the starting sheet adjacent to the loop was exposed to the deposition of copper, not only the loop, but also the sheet built up, making a good firm joint. After the adoption of this method, no further trouble was experienced with dropping sheets.

As previously mentioned, only about 45 to 50 per cent of the total acid used in an 8-day leach is utilized in dissolving copper. The remainder is used in dissolving impurities. If copper only is removed from the solution, the other substances will gradually accumulate and the solution will reach a condition where it will become sluggish in dissolving the copper from the ore. To keep the solution active, it is evident that a portion must be discarded and replaced with fresh water. The quantity of solution discarded per day must contain impurities equivalent to the amount dissolved per day, if the accumulation is to be avoided. In the experimental work it was found that, under similar conditions, nearly all the substances that went into the solution were present in a fairly constant ratio to one another. Of the various impurities dissolved, iron is the most easily and quickly determined and was used as the indication of the quantity of solution necessary to be discarded. The experimental work clearly demonstrated that the best results were obtained when the total iron in the solution did not exceed 2 per cent.

The original cementing equipment consisted of six sections of reinforced-concrete launders. These were arranged in two parallel rows of three sections each. The bottom of each launder sloped toward three side clean-out gates. The scrap iron rested upon a grated wood floor. The solution flowed through each one successively, but could be by-passed to allow the cleansing and refilling of any of the sections. From these launders the waste solution went to the desert.

Under good operating conditions practically all the copper was precipitated. When a launder was no longer efficient, the solution to that launder was by-passed and the solution remaining in it was drained. The cement copper was shoveled out onto wooden grates, where the iron was washed off with a hose, and the unconsumed iron was returned to the launders.

Cement copper when clean and finely divided dissolves readily in ferric sulphate, with the formation of copper and ferrous sulphates. By so doing not only is the cement copper dissolved, but the ferric iron is reduced also. The plan was to hose off the loosely adherent copper from the scrap iron to the bottom of the tank and then flush it into one or more circular lead-lined tanks, called agitators. These tanks are 20 ft. in diameter and 6 ft. deep, provided with a stirring device, driven by a small motor; 125 gal. per min. of tank-house return solution can be circulated through each tank.

This plan of redissolving the cement copper was carried out when the operating conditions of the plant required it. The principal objections to the continuous use of such a plant are that by redissolving the cement copper in tank-house solution the total copper output of the plant is reduced, which at times does not give the greatest profit possible. Although the Ajo plant is history, this lengthy description is given as it details the operation of a plant, the details of which were carefully planned, and which functioned profitably to the exhaustion of the deposit.

Union Minière du Haut Katanga.—Sulphuric acid leaching was practiced for a time on the shale ores of the Union Minière du Haut Katanga. The plant presented

some novelties as compared with other installations, in that continuous and not batch leaching was employed; the leaching was by agitation instead of percolation; washing the sand tailings was carried on in multideck Dorr classifiers arranged countercurrent; washing the slime tailings was performed continuously in thickeners; the iron and alumina in the solutions were held within reasonable limits by continuous purification through neutralization of a part of the solution with original ore or concentrates[36].

Some condition was present, which has never been satisfactorily explained, that quickly ate away any copper alloys, and only lead, duriron, some of the chrome-nickel irons, rubber, asphalt mastic, glass, and porcelain could safely be used in contact with the solutions. This was possibly due to cobalt.

The removal of iron and alumina by precipitation with a portion of the ore was the first successful application of this idea to commercial practice. A portion of the solution was constantly withdrawn and agitated for 17 hr. with raw ore or concentrates, completely neutralizing it. The pulp was then classified, the sands were sent back to the leaching circuit, and the slime was sent to a thickening-washing circuit which was always maintained at neutrality. The washed slime discarded from this operation ran about 1 per cent Cu, but apparently it was figured that control of the iron and alumina was worth this price.

Andes Copper Co.—The leaching plant of the Andes Copper Co. at Potrerillos, Chile, is a sulphuric acid leaching operation, a 6-day countercurrent leaching followed by a 1-day countercurrent wash. The operation is unique in that through a complete neutralizing with 200-mesh limestone the entire leach solution is purified from iron, alumina, arsenic, and phosphorus before it goes to the tank house. This means that all the free acid in the leach solution and that combined with the iron and alumina is thrown down as calcium sulphate and is eliminated along with these impurities. This consequently means that about 63 lb. of 60° sulphuric acid is required per ton of ore treated. This acid is produced by treating a part of the gases from the roasting plant for the production of sulphuric acid[38].

The first leach of the ore is by upward percolation, but the succeeding five leaches are by downward percolation. The tanks are concrete with mastic floors and acid-proof brick walls. The filter bottoms are of the Inspiration type.

It was found necessary to remove the slimes which run approximately 5½ per cent and to treat them by agitation. Any discard and excess wash solutions are treated with crushed limestone by agitation at about 37°C. The precipitated copper carbonate and the accompanying calcium sulphate are fed back into the purifiers, the copper carbonate acting in the same way as does the limestone to neutralize acid and throw down iron and aluminum.

Chlorine is eliminated by agitating the purified leach liquor with excess of cement copper, which throws down much of the chlorine as cuprous chloride. The settled residue consisting of cuprous chloride and cement copper is treated with ferrous-chloride solution, which dissolves the cuprous chloride. The copper in this solution is precipitated with scrap iron, washed, and used for further dechloridizing. The copper is then precipitated from the dechloridized solution by electrolysis, using 15 per cent antimonial lead anodes. The copper is reduced to about 11 g. per l. in the tank house, the spent electrolyte going back to the leaching tanks.

Inspiration Consolidated Copper Co.—The Inspiration Consolidated Copper Co. in October, 1926, commenced large-scale leaching of an ore carrying oxidized copper and chalcocite by the use of ferric sulphate and sulphuric acid. After 2 years a flow sheet was adopted in which slime was removed, treated first by flotation, then by agitation, while the sands were treated by upward percolation. The lixiviant was regenerated by electrolytic precipitation. The solution from the tank house carried about 9 g. per l. of iron, 41.1 g. of acid, 21.6 of copper (in 1931); the ferric iron in the

solution from the leaching tanks ran 2.8 g. per l., but by the time it went to the tank house it carried 4.0 g. of ferric iron (total iron, 20 g.). The solution to the tank house carried 26.4 g. of copper (1931). The anodes are 8 per cent antimonial lead. Starting sheets for the tank house are made in a small section of the tank house using anodes cast at the Inspiration smeltery, near by. It was found highly advantageous to warm the solutions so that they went on the ore at 42°C. Wash waters or waste solutions were treated with detinned scrap before discarding[37].

BIBLIOGRAPHY

1. LINDGREN: *U. S. Geol. Survey Prof. Paper* 43.
2. CHANNING, J. PARKE: Extracting Copper from Ore in Place, *Eng. Mining Jour.*, Mar. 25, 1911.
3. ARGALL, PHILIP: The Recovery of Copper from Mine Drainage, *Mining Sci. Press*, May 12, 1906.
4. IRVING, JOSEPH W.: Heap Leaching of Low-grade Copper Ores, *Eng. Mining Jour.-Press*, Apr. 29, 1922.
5. DE KALB, COURTNEY: Metallurgical Methods at Rio Tinto, *Eng. Mining Jour.-Press*, Feb. 5, 1921.
6. OLDRIGHT, GEORGE L.: Leaching of Caved Areas in Ohio Copper Mine, Bingham, Utah, *Mining Met.*, October, 1923.
7. WORMSER, FELIX E.: Leaching a Copper Mine, *Eng. Mining Jour.*, Oct. 20, 1923.
8. POSNJAK, E.: Acceleration of Rate of Oxidation of Ferrous Iron, and Its Application to Heap Leaching, *A.I.M.E. Tech. Pub.* 1615-B-E, December, 1926.
9. HUDSON, A. W., and G. W. VAN ARSDALE: Heap Leaching at Bisbee, Ariz., *Trans. A.I.M.E.*, 1923.
10. TOBELMANN, H. A., and JAMES A. POTTER: First Year of Leaching by the New Cornelia Copper Co., *Trans. A.I.M.E.*, 1920.
11. ALLEN, A. W.: Development of the Disc Crusher and Leaching Practice, *Mining Jour.*, Dec. 7, 1921.
12. MIDDLETON, PERCY: On Sulphatizing Roasting of Semioxidized Copper Ores, *Eng. Mining Jour.-Press.*, Sept. 9, 1922.
13. BENEDICT, H. C.: Ammonia Leaching of Calumet Tailings, *Eng. Mining Jour.*, July 14, 1917.
14. BENEDICT, H. C., and H. C. KENNY: Ammonia Leaching of Calumet and Hecla Tailings, *Trans. A.I.M.E.*, 1924.
15. EDDY, LAWRENCE: Practical Considerations in Ammonia Leaching of Copper-bearing Ores, *Eng. Mining Jour.*, Apr. 1, 1919.
16. LAWRENCE, HORACE M.: Ammonia Leaching of Copper Tailings at Kennecott, *Eng. Mining Jour.*, Nov. 3, 1917.
17. U. S. patent 1440186, December, 1922.
18. JENNINGS, E. P.: The Neill Process at Coconino, Ariz., *Eng. Mining Jour.*, Jan. 18, 1908.
19. VAN BARNEVELD, CHARLES E., and EDMUND S. LEAVER: Leaching Non-sulphide Copper Ores with Sulphur Dioxide, *U. S. Bur. Mines Tech. Paper* 312.
20. LEAVER, EDMUND S., and R. V. THURSTON: Ferric Sulphate and Sulphuric Acid from Sulphur Dioxide and Air, *U. S. Bur. Mines Repts. Investigations*, Dec. 1, 1923.
21. RANKIN, H. D.: U. S. patent 1150787, Aug. 17, 1915.
22. WESTBY, GEORGE C.: Nitric Acid and Copper Ore, *Eng. Mining Jour.*, Mar. 15, 1918.
23. IRVING, JR., JOSEPH: Leaching Ore with Sulphur Dioxide, *Eng. Mining Jour.*, Aug. 26, 1922.
24. AUSTIN, W. L.: *Mining Methods*, September; November, 1910.
25. *Trans. A.I.M.E.*, Vols. 10 and 16.

26. HOFFMAN, OTTOKAR: U. S. patent 634751, Oct. 10, 1899.
27. POPE, F. W., and A. W. HAHN: U. S. patent 1232080, July 3, 1917.
28. VAN ARSDALE, GEORGE D.: U. S. patent 723949, Mar. 31, 1903.
29. GREENAWALT, W. E.: The Greenawalt Electrolytic Copper Extraction Process, *Trans. A.I.M.E.*, 1924.
30. EICHRODT, C. W.: Electrolytic Tank House, Chile Exploration Co., Chuquicamata, Chile, *Trans. Am. Electrochem. Soc.*, 1924.
31. LONGMAID-HENDERSON Process, Lunge, "Treatise on the Manufacture of Sulphuric Acid and Alkali," Vol. 1.
32. VAN DER POEL, C. S.: Metallurgical Operations at Bwana M'Kubwa, paper presented at the Third Empire Mining and Metallurgical Congress, South Africa, 1930.
33. SULLIVAN, JOHN D.: Chemical and Physical Features of Copper Leaching, Rocky Mountain Fund Volume on Copper Metallurgy, *Trans. A.I.M.E.* Vol. 106, pp. 515-546, 1933.
34. DUGGAN, E. J.: Ammonia Leaching at Kennecott, *Trans. A.I.M.E.*, Vol. 106, pp. 547-558, 1933.
35. CAMPBELL, T. C.: A Brief Description of the Reduction Plant of the Chile Copper Co., *Trans. A.I.M.E.*, Vol. 106, pp. 559-608, 1933.
36. WHEELER, ARCHER E., and H. Y. EAGLE: Development of the Leaching Operations of the Union Minière du Haut Katanga, *Trans. A.I.M.E.*, Vol. 106, pp. 609-649, 1933.
37. ALDRICH, HAROLD W., and WALTER G. SCOTT: The Inspiration Leaching Plant, *Trans. A.I.M.E.*, Vol. 106, pp. 650-677, 1933.
38. CALLAWAY, L. A., and F. N. KOEPEL: Metallurgical Plant of the Andes Copper Mining Co., *Trans. A.I.M.E.*, Vol. 106, pp. 693-728, 1933.
39. SULLIVAN, JOHN D., and G. L. OLDRIGHT: Leaching Oxidized Copper Ores: Effect of Strength of Acid, *U. S. Bur. Mines Repts. Investigations* 3106, July, 1931.
40. SULLIVAN, JOHN D., and KENNETH O. BAYARD: Extraction of Soluble Copper for Ores in Leaching by Percolation. *U. S. Bur. Mines, Repts. Investigations* 3073, April, 1941.
41. SULLIVAN, JOHN D., and ALFRED P. TOWNE: Leaching Copper Ores: Advantage of Wet Charging, *U. S. Bur. Mines Repts. Investigations* 3050, February, 1931.
42. SULLIVAN, JOHN D.: Factors Involved in the Heap Leaching of Copper Ores, *U. S. Bur. Mines Circ.* 6425, April, 1931.
43. THOMAS, ROBERT W.: Leaching Copper from Worked-out Areas of the Ray Mines, Arizona, *Mining Met.*, November, 1938, pp. 481-485.
44. TAYLOR, J. H., and P. F. WHELAN: Leaching at Rio Tinto, *I.M.E., Bull.* 457, November, 1942.
45. CADDICK, A. J.: Precipitation of Copper by Hydrogen Sulphide, *Mining Mag.*, Vol. 52, No. 1, pp. 20-30, January, 1935.
46. FLOE, C. F.: Extraction of Copper from Roasted Concentrates by Sulphuric Acid Baking, *A.I.M.E. Tech. Pub.* 768, February, 1937 meeting.
47. KISKA, F.: Langung kupferkaktiger Kiessalrände mittels schwefeliger Säure, *Metall u. Erz*, Vol. 32, No. 19, p. 459, Oct. 1, 1935.
48. DENNIS, W. H.: Copper Extraction by Leaching, *Indust. Chem.*, Vol. 18, No. 213, p. 393, October, 1942; Vol. 18, No. 219, p. 427, November, 1942.
49. JOHNSTONE, H. F., and R. W. DARBYSHIRE: Sulphur Dioxide as Raw Material, *Ind. Eng. Chem.*, Vol. 34, No. 3, 1942.
50. BENEDICT, C. H.: Quincy Tailing Treatment, *Eng. Mining Jour.*, Vol. 145, No. 4, pp. 74-78, 1938.
51. HUDSON, A. W.: *Mining Congr. Jour.*, Vol. 12, pp. 744-745, October, 1926.
52. SAWYER, E. M.: *Mining Congr. Jour.*, July, 1929, p. 539.

CHAPTER XIII

ELECTROLYTIC REFINING OF LEAD

BY GUSTAVE REINBERG¹

History.²—Commercial electrolytic refining of lead dates from the development of the fluosilicate electrolyte by Anson G. Betts, at the beginning of the twentieth century. Earlier experimenters had endeavored to use acetate or nitrate solutions, from which the lead was deposited at the cathode in the form of loose crystals or sponge, which fell to the bottom of the tanks or was removed by mechanical scrapers. The practical difficulties of this method of operation, especially those incident to the washing and melting of the refined lead, proved insurmountable. Betts[1] investigated a number of complex acids, including fluosilicic, fluoboric, dithionic, methyl and ethyl sulphuric, and several sulphonic acids, all of which formed very soluble lead salts and produced electrolytes of high conductivity. He found that by the addition of an organic colloid, such as glue or gelatin, these electrolytes could be made to produce a solid and adherent cathode deposit, with a density equal to that of cast lead. Considerations of cost and stability have made fluosilicate electrolytes the logical choice for refining operations, although fluoborates and sulphonates have had a limited application for special purposes such as electroplating.

The pioneer Betts process refinery, that of the Consolidated Smelting & Refining Co., Ltd., at Trail, B. C.[2] has been in continuous operation since 1903, and has been successively modernized and enlarged to a capacity in excess of 500 tons per day. The plant of the U. S. Smelting Lead Refinery Inc., at East Chicago, Ind., started operations in 1906 and has also been extensively modernized in recent years. The latest Betts refinery to be built is that of the Cerro de Pasco Copper Corp., at La Oroya, Peru, the first unit of which was started in 1934, followed by a large capacity enlargement in 1937. This plant was specially designed for the treatment of very impure bullion, and its operating conditions differ in several respects from previous practice[3].

The Betts process is notable for its ability to produce refined lead of exceptional purity, and is particularly adapted to the treatment of bullion containing bismuth, or in which the total content of impurities is large. It does not offer any significant metallurgical advantage over the older Parkes process for the refining of relatively pure bismuth-free bullion such as that produced from Missouri ores, but may have an economic advantage if fuel cost is high in comparison with electric-power rates.

Electrochemical Data.—As lead is divalent in fluosilicate solutions, the electrochemical equivalent is 3.865 g. per amp.-hr., or 0.2045 lb. per amp.-day. A current efficiency of 90 to 95 per cent of this figure is usually realized. The most economical current density will normally be between 15 and 18 amp. per sq. ft. The electrolyte composition may vary considerably, representative values being 80 g. per l. each of Pb and free H_2SiF_6 , corresponding to a total SiF_6 content of 135 g. per l. Electrolyte resistance varies with composition as shown in the attached curves (Figs. 1 and 2). This resistance also varies with temperature in the usual manner (Fig. 3). In tem-

¹ Metallurgical engineer, Cerro De Pasco Copper Corp., New York.

² References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

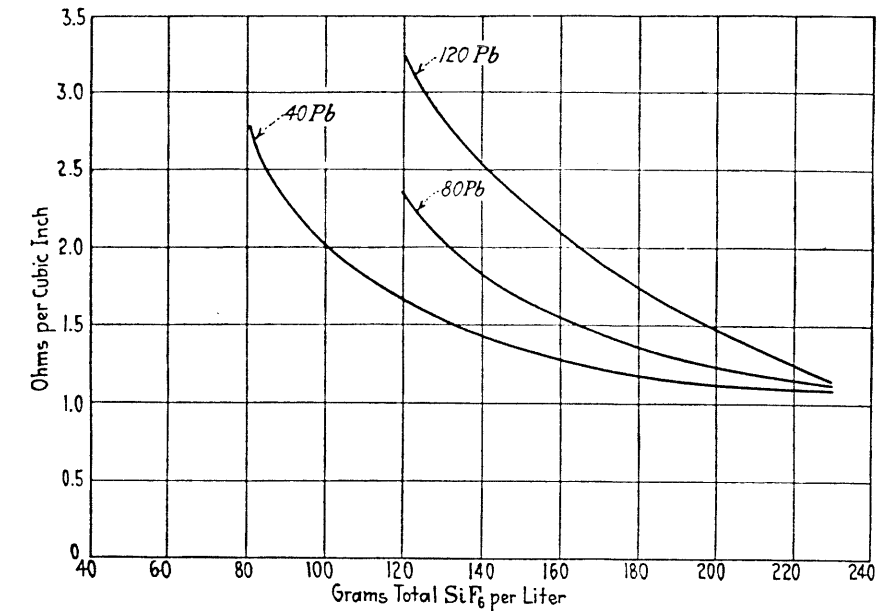


FIG. 1.—Electrolyte resistance curves.

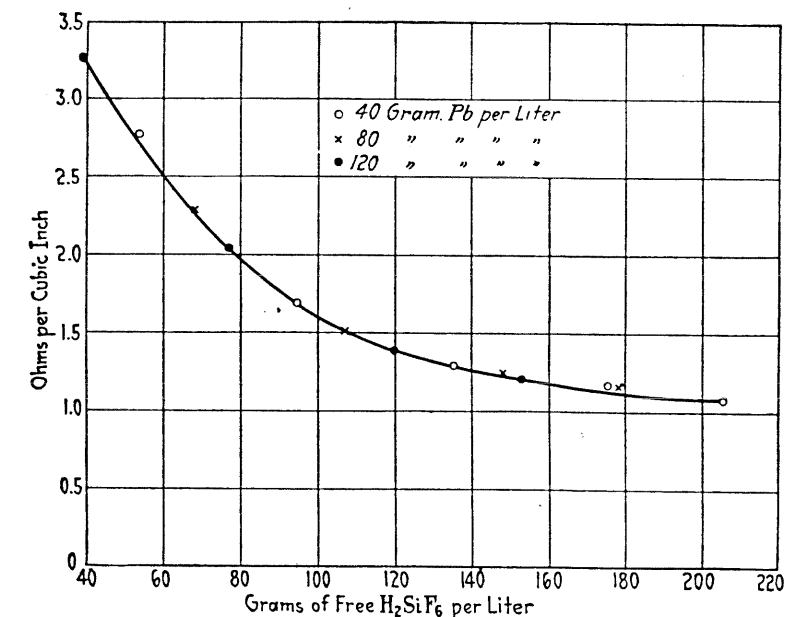


FIG. 2.—Ohms per cubic inch of electrolyte, varying the free H_2SiF_6 with 40, 60 and 80 g. of lead per liter.

perate climates, an equilibrium temperature will ordinarily be reached at some permissible value between 30 and 40°C., but in extremes of weather, some artificial heating or cooling may be required, since very low temperature would increase resistance unduly, and excessively high values might damage tank linings. Under these conditions of current density, electrolyte concentration, and temperatures, the average volts per cell will approximate 0.45, and the direct-current power consumed in the cell circuit will be about 120 kw.-hr. per ton.

Cell circuits have generally been designed for a total current of 4000 to 6000 amp. direct current. The over-all voltage of a 4500-amp. circuit is approximately equal, numerically, to its refining capacity in short tons of lead per day.

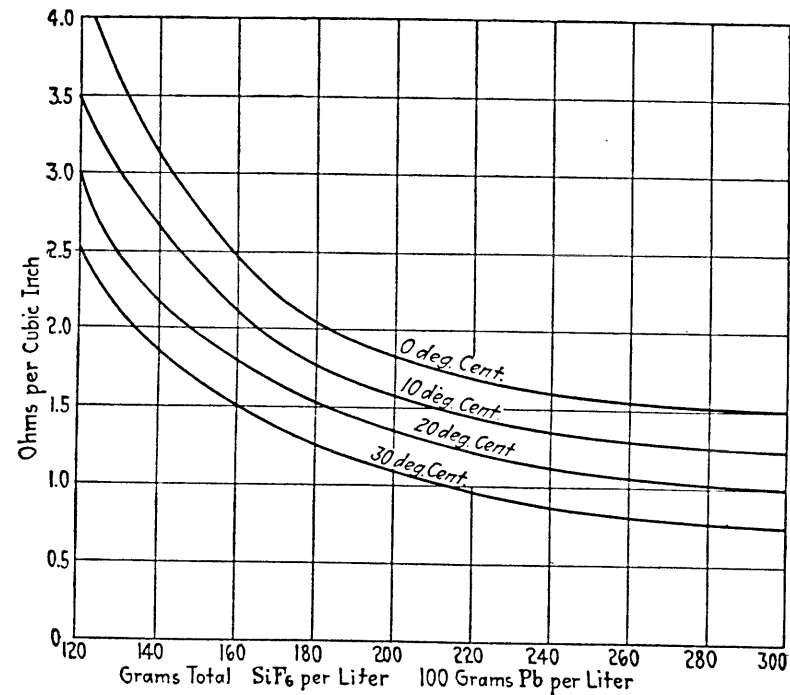


FIG. 3.—Temperature-resistance curves, fluosilicate electrolyte.

The amount of glue used as an addition agent ranges from 0.5 to 1.5 lb. per ton of lead produced. It has been found that bindarene flour (a by-product of the paper-pulp industry) may be substituted for half or two-thirds of the total glue used, the glue-bindarene mixture often producing a better deposit than can be obtained with glue alone. The addition agents are, for the most part, deposited with the lead and produce a characteristic odor when the cathodes are melted.

The metals having electromotive-solution potentials higher than lead, *i.e.*, Zn, Cd, Fe, Ni, and Co, are normally absent from lead bullion, or are present in such small amounts that no injurious accumulation in the electrolyte will occur. An electrolyte can therefore be used for many years without purification. Small accumulations of iron, alkali metals, and nitrogenous decomposition products of glue are found in old electrolytes, but usually have no harmful effect on the operation.

Tin presents a special case, in that its electrolytic solution potential is nearly identical with that of lead. It may therefore be dissolved and deposited with lead at the

cathode, if present in the anodes being refined. Tin which thus contaminates the cathodes is removed by mechanical dressing or blowing with air when the cathodes are melted. In general, a portion of any tin present in anodes will form intermetallic compounds with other impurities present, which lower its solution potential and cause it to be retained in the anode slime. If the bullion under treatment contains sufficient tin to warrant the recovery of this element, it may therefore be expedient to remove it by a high-temperature dressing operation[4] before casting the bullion into anodes, rather than to recover it from slimes and cathode dross. The codeposition of tin and lead from fluosilicate solution is employed as a commercial method for the production of solder[5].

It has been observed that thallium is another element with anomalous behavior, which may be only incompletely removed from lead by electrolysis. Thallium, however, will occur in lead bullion only under exceptional circumstances, even when the parent ores contain it, as it is practically completely eliminated from the lead blast furnace by volatilization.

The impurities ordinarily associated with lead, all of which have lower solution potentials than lead and remain undissolved at the anode during electrolysis, are As, Sb, Bi, Cu, Ag, Au, and Te. These impurities, if present in sufficient amount, form a highly porous layer or blanket of slime which remains attached to the face of the anode and retains the original shape and appearance thereof as the lead is dissolved. The solution filling the pores of the slime blanket, a volume which is of course equal to that of the lead that has been removed, is not by any means of the same composition as the freely circulating electrolyte. It consists, rather, of a nearly neutral solution of lead fluosilicate of high concentration. The voltage drop that appears across the slime blanket, which increases as corrosion of the anode proceeds, is produced by the ohmic resistance of the solution in the pore volume and by "concentration-cell" effect.

In modern practice, the working life of the anode is determined by the nature and amount of impurities present in the bullion treated. In this way the thickness attained by the slime blanket is limited to a value such that the maximum voltage drop across it is less than the electrolytic potential difference available for impurity separation, by a safe margin. For usual types of bullion and normal current densities, appropriate anode corrosion periods will range from 2-day anodes for bullion containing 90 per cent Pb or less to 6-day anodes for bullion containing 98 per cent Pb or more; the exact limits must in every case be established by trial. This technique has eliminated the difficulties encountered in earlier years, when heavy anodes with 8- or 10-day corrosion periods were universally employed. With these long corrosion periods, voltage drops were excessive unless the bullion treated was very pure, and with very pure bullion, the slime blanket was too soft to be thoroughly adherent. In either case, the purity of the lead produced was adversely affected. The minimum amount of impurity that will produce a slime of satisfactory physical characteristics is dependent on the chemical composition of the slimes as well as other factors. This point requires careful attention if the bullion contains over 97 per cent Pb, and in certain cases, impurities may have to be recirculated to maintain proper conditions.

It is preferable to limit the maximum life of the cathodes to a 4-day period. Five- or six-day cathodes have been occasionally employed, but the increased weight and roughness of the deposit are serious handicaps. To facilitate cell-changing operations, the cathode life should be a factor or a multiple of the anode life, therefore 3-day cathodes would be used with 3- or 6-day anodes and 4-day cathodes with 2- or 4-day anodes.

Manufacture of Electrolyte.—Fluosilicic acid, H_2SiF_6 , which is also known as hydrofluosilicic acid, is obtained as a by-product in the manufacture of superphosphate

fertilizer; it may also be prepared by dissolving finely ground silica in hydrofluoric acid of about 40 per cent strength. Either percolation towers or agitator tanks may



FIG. 4.—Night view of Betts tank house; dip washing tanks for corroded anodes in foreground.

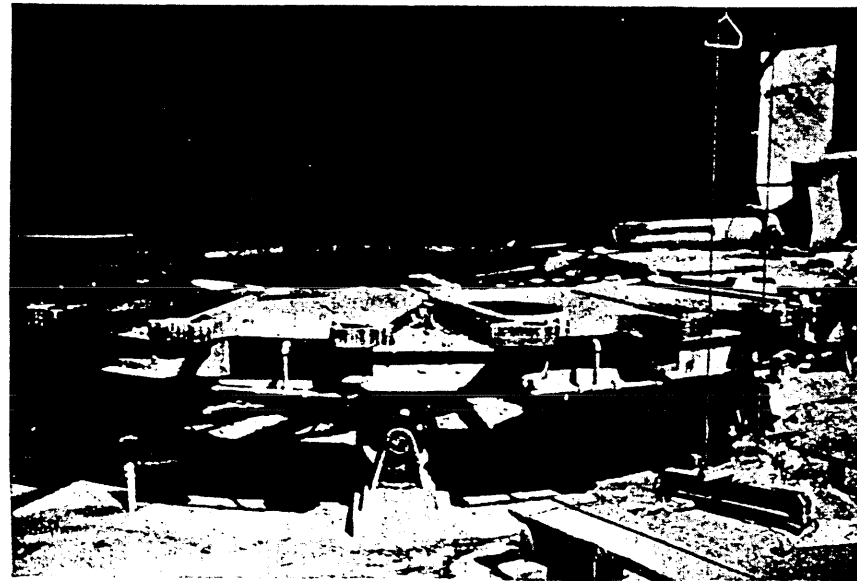


FIG. 5.—Anode-casting wheel with meter type of pouring device.

be employed for this purpose. An excess of silica must be used and the operation finished at an elevated temperature to secure complete conversion. The hydrofluoric

acid is produced by distillation from a mixture of ground acid-grade fluorspar and 66°Bé. sulphuric acid. Continuous equipment has been developed for this operation, but the original method of batch distillation from cast-iron retorts connected to water-cooled lead condensers is still used to a limited extent.

Lead fluosilicate may be prepared by dissolving lead carbonate or white lead in fluosilicic acid, but when required in quantity, as for the initial filling of a refining circuit, it is preferable to use electrolytic dissolving cells. These are horizontal cells with pig-lead anodes covering the bottom area and a perforated lead cathode suspended near the top. Acid is fed at a slow rate to the top of the cell, and the lead fluosilicate, which stratifies in the lower portion of the electrolyte by virtue of its high specific gravity, is removed through a siphon overflow. A current density of 30 to 50 amp. per sq. ft. of anode surface is suitable for these cells.

Acid Loss.—Under proper operating conditions, the over-all loss of fluosilicic acid from the electrolyte will not exceed 3 lb. of H_2SiF_6 per ton of refined lead produced.

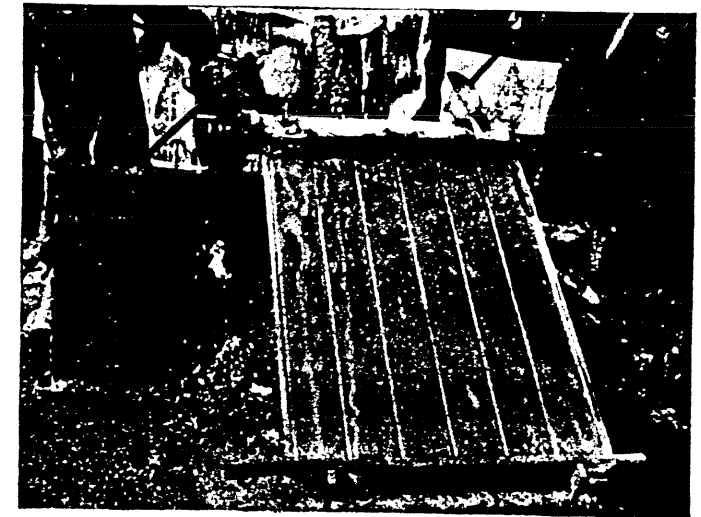


FIG. 6.—Starting-sheet pouring table, with integrally cast type of cross rod at bottom.

Much larger losses were at one time experienced, especially when relatively impure bullion was treated. These excessive losses have been eliminated by fundamental improvements in refinery construction and operating procedure.

In the first place, all mechanical losses, such as those due to inadequate cell construction, have been prevented. Limitation of the corrosion period eliminates decomposition loss at the anode and the formation of insoluble compounds such as antimony fluosilicate. Finally, and most important, is the complete recovery of solution entrained in anode slimes. Washing of the slimes must be conducted in counter-current fashion in order to avoid the necessity for any evaporation of wash liquors. Further, the more concentrated solutions must at all times have sufficient free acid present to prevent decomposition by hydrolysis. The most effective method of washing involves the use of diffusional processes, by which the slimes are completely washed before their removal from the surface of the anode scrap[3, 6]. This is accomplished by advancing the corroded anodes through a series of dip tanks, in which they remain for a sufficient period to attain equilibrium with successively decreasing concentrations of acid and wash water. This procedure is applicable only when the anodes contain sufficient impurities to produce a perfectly adherent slime blanket.

In normal operation, the lead content of the electrolyte increases slowly, in spite of the fact that the acid losses occurring are largely in the form of lead fluosilicate; this is due to the fact that the current efficiency is slightly lower at the cathode than at the anode, and to the small amount of lead that is dissolved chemically from the electrodes. To maintain normal composition, this excess lead is periodically removed, usually by the addition of sulphuric acid. An alternate method of lead removal is to electrolyze with graphite anodes, whereby lead peroxide is deposited at the anode while metallic lead is deposited at the cathode. Occasionally, however, a decrease in the lead content of an electrolyte may occur in operation, which is almost infallibly a danger signal indicating that an abnormal acid loss also prevails.

Construction and Operation.—Cells built of reinforced concrete have replaced the wooden tank construction originally used. They may be lined either with asphalt,

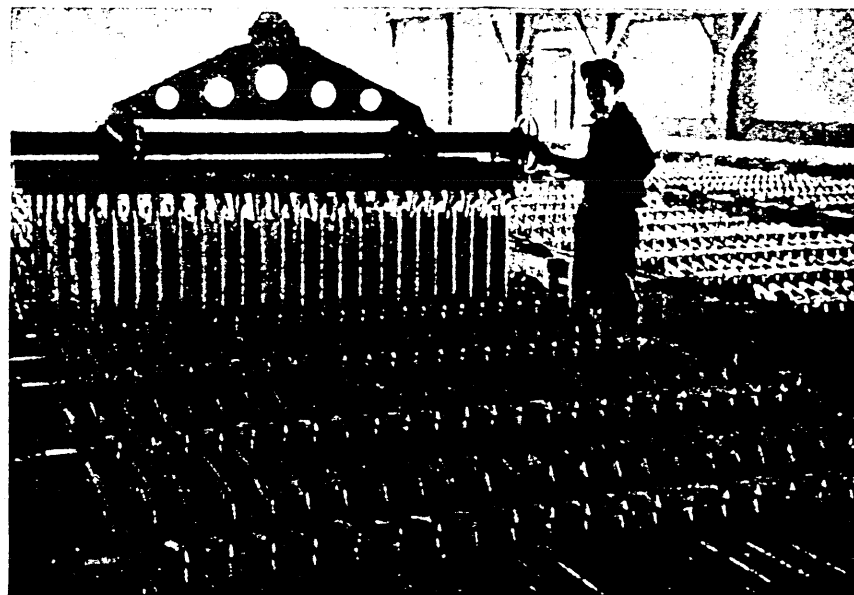


FIG. 7.—Corroded anodes being removed from cell, with short-circuiting bar in position at right end of tank.

resinous organic compounds, or by a recently developed method of impregnation with hot paraffin. Cells are arranged in cascade at the Trail plant; others use the side-by-side arrangement of the Walker system. Electrolyte is circulated at a rate of 2 to 5 gal. per min. per cell, usually entering the cell at the top and overflowing through a hard-rubber pipe extending within a few inches of the bottom. Centrifugal pumps of bronze or rubber-lined construction are used for electrolyte handling. Rubber-lined steel pipe is most satisfactory for cell feed lines, and rubber-lined launders for overflow return.

Anodes are cast in open horizontal cast-iron molds, which are generally mounted on a mechanically driven casting wheel. They are normally 24 to 26 in. wide by about 36 in. deep in body dimensions, with integral lugs or ears for suspension and handling. The thickness required, at usual current densities, is about $\frac{1}{8}$ in. per day of anode life, plus $\frac{1}{8}$ in. for the residual core sheet. It is important that anodes are cast to uniform weight and even thickness, in order to avoid excessive scrap and still ensure an unbroken core sheet at the end of the corrosion period. This requires a smooth-

running casting wheel with a rigid deck, molds carefully leveled, and, preferably, an automatic metering type of pouring device. The anode scrap, which is approximately 40 per cent with 4-day anodes, is of course remelted and cast in the same manner as the original bullion. At the tank house, the anodes are placed in racks in which they are properly spaced for transfer to the cells, the usual spacing being 4 to $4\frac{1}{2}$ in. center to center.

Cathode starting sheets are made by pouring a small quantity of refined lead from a tilting trough on to a cast-iron plate set at a small angle to the horizontal, on which the lead freezes in a uniform sheet about $1\frac{1}{2}$ in. thick. These sheets are supported in the cells from cross rods of hard-drawn copper to which they are attached by looping and spot-welding. Alternatively, the cross rod may be formed of copper-plated steel, with a dovetail slot into which the sheet is integrally cast. Starting sheets may be

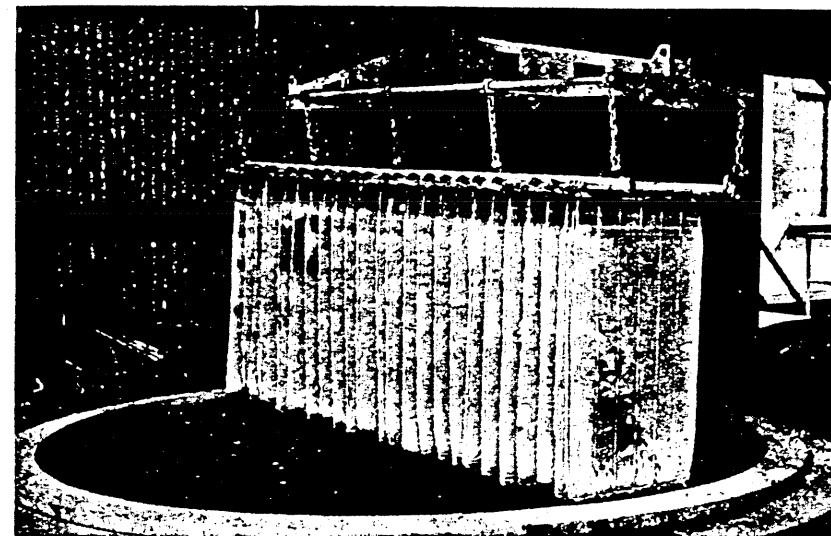


FIG. 8.—Cathodes being lowered into refined lead kettle.

stiffened considerably by grooving the casting table to form shallow corrugations, but at best are flimsy and require manual straightening before hanging in the cells. It is customary to fold over a small diagonal flap at each bottom corner of the sheet at the same time.

The deposited cathodes, weighing about 150 lb. each, are washed in a dip tank or by sprays upon removal from the cells and charged to welded steel melting kettles of 70 to 235 tons capacity. If integrally cast cross rods are used, these are skimmed from the surface of the lead after melting. Each kettle lot of refined lead is stirred or air-blown at 520°C . to remove glue ash and traces of residual impurities, sampled, and cast into standard bars of approximately 100 lb. Vertical centrifugal pumps are used to transfer the lead to the casting wheel. Casting temperatures may range from 375 to 425°C . From $1\frac{1}{2}$ to 2 per cent of oxide dross is produced in the melting and casting operation, which is either returned to a smelter or reduced to common lead in a small reverberatory furnace.

Both anodes and cathodes are handled to and from the cells in complete sets, usually 24 anodes and 25 cathodes, by overhead traveling cranes provided with special hooks, the cells being short-circuited individually for the few minutes required for this operation. At infrequent intervals, cells must be shorted out of the circuit for a

sufficient time to permit draining, cleaning, and inspection of the lining. If production schedules permit, an entire cell block or group is usually cut out together for this purpose.

Corroded anodes are advanced through the wash tanks by overhead cranes, if dip washing is used, the spacing between anodes being first closed up to permit four sets of anodes to be handled together. The slimes are then removed by passing them between revolving fiber brushes or by scraping and brushing in the case of very hard slimes. If dip washing is not practiced, the slimes must be brushed off in a tank of electrolyte and carefully washed by countercurrent decantation. The washed slime may be dewatered in a filter press or centrifuge, and further dried to a moisture content sufficiently low to permit charging to the melting furnaces. In the case of dip-washed slimes, the slurry from the brushing machine is fed directly to a steam-heated atmospheric double-drum drier, which reduces moisture content to a low percentage in a single operation. Briquetting the slimes under heavy pressure at this point will increase the efficiency of the subsequent melting operation, but this practice has not yet been applied commercially.

Precious metal recovery

Slime Treatment.—The details of subsequent slimes treatment are naturally variable, being determined by the composition and relative importance of the contained values. A number of wet methods of treatment have been proposed, but none has been widely used. When, as is often the case, the precious metal values are the primary concern, the general procedure is as follows: The slime is melted in a reverberatory furnace and the metal transferred to a furnace with submerged tuyères and blown with air. The major portion of the arsenic and antimony is thus removed by volatilization as oxide fume, which is collected in a baghouse connected to the flue system. Slags removed from the early stages of the operation contain the remainder of the arsenic and antimony and the majority of the lead present; as the oxidation proceeds, the residual lead is slagged off together with bismuth, copper, and tellurium. The final stages of the oxidation are conducted in a separate furnace, in which the tuyères may be above the metal bath, and to finish the charge, soda ash and niter are added to complete the removal of the tellurium and copper. A doré bullion assaying at least 99 per cent silver plus gold is tapped from this furnace and cast into shapes suitable for acid or electrolytic parting. The slags and baghouse fume are re-treated separately for recovery of their contained values, including the small proportion of the silver and gold which they carry. Slags from certain stages of the oxidation are often segregated to facilitate recovery of a particular element, such as bismuth.

Electrochemical Series.—Reference has been made in this chapter several times to the electrochemical position of the elements. In the following arrangement each element is electronegative to those that follow and electropositive to those that precede it: Cs+, Rb, Na, Li, Ba, Sr, Ca, Mg, Al, Cr, Mn, Zn, Ga, Fe, Co, Ni, Tl, In, Pb, Cd, Sn, Bi, Cu, H, Hg, Ag, Sb, Te, Pd, Au, Ir, Rh, Pt, Os, Si, C, B, N, As, Se, P, S, I, Br, Cl, O, F—. The order varies slightly according to the acid radical and according to dilution, but it is a good guide for experimental work.

REFERENCES

1. BETTS, A. G.: "Lead Refining by Electrolysis," 1908.
2. *Trans. A.I.M.E.*, Vol. 121, p. 271, 1936.
3. *Trans. A.I.M.E.*, Vol. 121, p. 283, 1936.
4. U. S. patent 2155545 (1939).
5. U. S. patent 1842028 (1932).
6. U. S. patent 1913985 (1933).

CHAPTER XIV

THE ELECTROLYTIC ZINC PROCESS

BY FREDERICK LAIST,¹ RUSSEL B. CAPLES,² AND GUY T. WEVER³

Definition.—Metallic zinc is extracted from its ores by two main methods, pyrometallurgical and hydroelectrometallurgical. The older pyrometallurgical operation, commonly referred to as the "retort process," depends on the reduction of zinc oxide to the metallic state by carbon. The hydroelectrometallurgical operation, commonly referred to as the "electrolytic-zinc process," is a much later development in which roasted zinc ores are leached in dilute sulphuric acid and the zinc obtained in the metallic state by electrolysis of the resulting solution. Zinc produced by this method is called "electrolytic zinc" to distinguish it from the "retort zinc" produced by the retort process. *cash*

The electrolytic-zinc process was originally confined to the complex lead-silver ores of zinc not well suited to the retort process. Further developments of the process have enabled it to be applied to almost any type of zinc ore.

Many variations of the electrolytic process have been investigated, both as to the zinc salt to be electrolyzed and as to the method of preparing the solution. The only successful large-scale operations have used dilute sulphuric acid leaching and electrolysis of the resulting zinc sulphate solution. This method is cyclic in that it uses the dilute sulphuric acid formed during the electrolysis of zinc sulphate solution as the source of acid for leaching additional material. The use of zinc chloride solution in the electrolytic-zinc process has never met with any outstanding success. The only commercial unit of this kind was the small plant of Brunner, Mond and Co., England, operated between 1896 and 1924, with a capacity of 5 to 10 long tons of zinc per day. Since that time no commercial plant has operated using zinc chloride solutions. Several companies have experimented with the electrolysis of fused zinc chloride; but this method has never been found satisfactory.

History.—It has been known for more than 75 years that zinc could be deposited from its solutions by electrolysis, but no attempt was made to apply this knowledge on a large scale as a method for producing zinc from its ores until about 1880. Processes employing both zinc chloride and zinc sulphate solutions were tried from time to time without marked commercial success. In 1914, the Anaconda Copper Mining Co. at Anaconda, Mont., and the Consolidated Mining and Smelting Co. at Trail, B. C., began independent investigations of the process as a means of solving the problem of treating complex ores occurring in their respective districts. Both were sufficiently successful to justify the erection of small test plants which were rapidly enlarged as the war demand for high-grade zinc developed. Later, the Australian zinc producers were attracted by the successes of these companies and, after a thorough investigation of the process and of the results obtained, built a plant at Risdon, near Hobart, Tasmania, for the treatment of concentrate from the Broken Hill mines.

The original plant of the Anaconda Copper Mining Co. at Anaconda, Mont., was more of a pilot plant for the development of the process than a commercial unit,

¹ Vice-president in charge of Metallurgical Operations, Anaconda Copper Mining Co., New York.

² Manager, Great Falls Reduction Department, Anaconda Copper Mining Co., Great Falls, Mont.

³ Superintendent of Indium and Rare Metals Department, Great Falls Zinc Plant, Anaconda Copper Mining Co., Great Falls, Mont.

but before dismantlement it was producing more than 25 tons of zinc per day. A plant having a capacity of 100 tons per day was constructed at Great Falls, Mont., in 1916. The Great Falls plant was located near the source of power, because it was more economical to transport the materials to be treated than to transmit the power. Shortly after the Great Falls plant started operations, the pilot plant at Anaconda was abandoned. The capacity of the Great Falls plant has been steadily increased until at the present time it is capable of producing more than 300 tons of slab zinc per day. The demand for zinc was such that a plant with a capacity of 150 tons per day was built at Anaconda early in 1928. This plant has also been enlarged in recent years.

The original 60-ton plant of the Consolidated Mining and Smelting Co. at Trail, B. C., has been enlarged until it is now one of the largest producers of zinc in the world.

The Amalgamated Zinc Co. first operated a small test plant at Bully Hill, Calif., the material treated being concentrate shipped from Australia. This work was the basis for the construction of a 10-ton unit at Risdon, by the Electrolytic Zinc Co. of Australia. After a year or so of operating this plant, it was decided to abandon it and construct a 100-ton plant. The Risdon plant is now ranked among the larger zinc producers.

These companies were the pioneers in the successful commercial application of the electrolytic-zinc process, and all use the same basic process. These plants have found that, for the electrolysis of zinc sulphate solution, a normal current density of 30 to 40 amp. per sq. ft. of cathode surface is the most satisfactory for their particular needs. This is considered a low current-density operation.

After these plants had demonstrated the commercial success of the process over a period of 10 years, many new plants were built in widely scattered parts of the world. Most of these plants employ processes closely resembling those developed in the pioneer plants.

The Sullivan Mining Co. operates a plant of considerable capacity near Kellogg, Idaho.¹ The outstanding feature of this plant is that it uses the Tainton high-density high-acid process. Shortly after this plant was completed, the Evans-Walloway plant, at East St. Louis, Ill., was built. This plant, also using the Tainton process, was operated for only a short time. In 1940 it was rebuilt by the American Zinc Co. for a low-acid low-density process as in general use elsewhere.

The early attempts to use sulphuric acid leaching were failures mainly because the experimenters failed to realize that a very high purity of solution was necessary for the successful electrolysis of zinc-sulphate solution. Once this fact was recognized, and suitable methods of purification were developed, the ultimate success of the electrolytic-zinc process was assured. Many important details remained to be worked out, but the fact that, with a sufficiently pure solution, zinc could be successfully deposited from an acid solution gave the process enough promise to justify the expense of developing the necessary methods.

Most electrolytic-zinc plants follow the same basic methods, but are highly individualistic in their applications of the process. The problems encountered by

¹This plant is often referred to as the Silver King plant, because of its situation. The original plant was described by U. C. Tainton and E. T. Leyson in Vol. 70, *Trans. A.I.M.E.*, p. 496, 1924. In Vol. 121, p. 527, 1936. W. G. Woolf and E. R. Crutcher bring the information concerning this plant up to that date. There have been various high-density plants built here and abroad since the original Sullivan installation, one of the most recent being that at Corpus Christi, Tex., which has been well covered by G. H. Cunningham and Allen C. Jephson in Vol. 159, *Trans. A.I.M.E.*, p. 199, 1944. If detailed information on the high-density zinc process is desired, the reader is referred to these articles and to the *Eng. Mining Jour.*, Vol. 145, No. 9, pp. 64-72, 1938.—EDITOR.

each plant are so different from those of any other plant that there remains no "standard" practice that might be used as a basis for comparison.

Application of the Process.—The original idea in developing the electrolytic-zinc process was to provide a method for the treatment of complex zinc ores. Those ores were mainly lead-zinc-silver ores, most of which also contained some copper and iron and produced a concentrate rather low in zinc content—30 to 40 per cent. These concentrates were not well suited to the retort process. There is now no doubt of the superiority of the electrolytic process for the treatment of ores of this class where power is available at a comparatively low rate. Higher recoveries of all metals present and lower operating costs per pound of zinc are the two main advantages of this process.

The concentrates originally treated at Anaconda and Great Falls contained less than 35 per cent zinc and about 15 per cent iron. Improvements in concentration practice since that time have made possible the separation of zinc and lead in many ores of this class, with the production of a much higher grade zinc concentrate. This higher grade concentrate contains much less lead, iron, and silver than formerly encountered and has proved particularly adaptable to the electrolytic process.

One essential requirement of the electrolytic process is a large source of power, the cheaper the better. Most of the large electrolytic-zinc plants have been located close to the source of comparatively cheap water power. Power is the largest single item of cost in the operation, and it is necessary to obtain the lowest rate possible. The lower the rate of power, the wider the range of ores that can be economically treated. It is not vitally necessary that water power be available, as cheap power can be generated from coal in some localities and then transmitted to the source of ore supply. The saving of freight on both ore and coal can then be applied as a credit to the cost of producing power. The amount of coal and coke required by a retort plant using coal for fuel is just about sufficient to produce the power required for an electrolytic plant of the same capacity. Within reasonable distances, it is cheaper to generate power at the source of fuel and transport it to the ore supply, than it is to ship the coal. Water power is in most cases cheaper than power generated from coal, but usually it must be developed in large units to be economical. It may be that some possible sources of water power, not now utilized because of the lack of sufficient demand near by, may eventually be developed for the location of electrolytic-zinc plants. The total requirement for a plant producing 100 tons of electrolytic zinc per day is about 20,000 hp.

From the standpoint of labor requirements and working conditions, the electrolytic process compares favorably with the best of the industrial plants. For the production of 100 tons of zinc per day from a concentrate containing 55 per cent zinc, less than 200 men are required. A large number of these are comparatively unskilled labor. A high class of labor is attracted, making for a steady and dependable supply of labor of more than average efficiency.

The cost of construction of an electrolytic-zinc plant is necessarily high, owing to the large amount of copper, lead, and aluminum required for bus-bar lines, electrodes, electrode support bars, solution piping, acidproof pumps, and other acidproof equipment. The high salvage value of an electrolytic-zinc plant offsets the heavy first cost. The cost of buildings for an electrolytic-zinc plant need be no more than for a retort plant of like capacity. The difference in cost between the two is mainly for the equipment contained in the buildings. When the high salvage value of an electrolytic plant is credited to the cost of construction, the ultimate difference in cost between it and a retort plant will be little, if any, in favor of the retort plant.

The normal production of a high-purity zinc is a large factor in favor of an electrolytic-zinc plant. Zinc of high purity usually commands some premium over the

Foot.
p. 1
of zinc

lower grades. It is possible for an electrolytic plant to furnish zinc of any specified analysis, varying either the cadmium or lead content to suit the customer. Any grade up to the "electrolytic" grade with a purity of 99.99+ per cent can be produced. In fact it is quite common for an electrolytic plant to produce all its cathode zinc with a high degree of purity and to debase a portion with cadmium or lead during melting and casting, in order to meet customers' specifications.

The high recovery of metals other than zinc by the electrolytic process, and the comparatively small amount of residue produced, will, in some cases, result in the production of a residue of sufficient value to pay the cost of treatment. A high recovery of lead from electrolytic-plant residue may be obtained at moderate cost, and with some ores, the credit from residue may amount to a large item in favor of the electrolytic process.

Combinations of circumstances are possible that will eliminate either the electrolytic or the retort process from consideration for the treatment of any class of ores in any locality; so both processes should be thoroughly investigated.

The large amount of soluble silica in carbonate and silicate ores is decidedly detrimental to the electrolytic-zinc process, making the separation of residue and solution a difficult problem. This problem has been successfully met by the plant of the Rhodesia Broken Hill Development Co., Broken Hill, Northern Rhodesia. This plant produces zinc by the electrolytic process from ore containing 25 per cent zinc in the form of silicate. The outstanding feature of the process used is the conditioning of the leach pulp, by careful control of temperature and acidity, to convert the gelled silicic acid into the granular form.

There are isolated instances in which certain impurities, such as arsenic, antimony, cobalt, nickel, and germanium, occur in such amounts as to add greatly to the cost of solution purification in the electrolytic-zinc process. These classes of ores can be more economically treated by the retort process.

The electrolytic process is particularly suited to the treatment of concentrates produced by the flotation method. The smaller the particle size of the concentrate to be roasted, the lower the temperature necessary to eliminate the sulphur content. Also, finely ground calcine is essential for the satisfactory leaching of roasted concentrate. A large proportion of zinc concentrate now produced is flotation concentrate, especially since the general application of selective flotation to ores containing both zinc and lead.

Outline of the Process.—An arbitrary division of the electrolytic-zinc process groups the necessary operations under three divisions: (1) the preparation of ore or concentrate for leaching, (2) the treatment of roasted ore or concentrate to produce a pure solution of the zinc salt to be electrolyzed, and (3) the electrolysis of the pure solution to produce metallic zinc and to regenerate the leaching solution.

Preparation of Concentrate for Leaching.—Concentrates containing zinc sulphide must be roasted to convert the zinc sulphide present into zinc oxide or zinc sulphate. Zinc sulphide is insoluble in the leaching solution, while zinc oxide or zinc sulphate is readily soluble. The conditions under which roasting is carried on also control to some extent the solubility of iron, copper, and silver in the leaching solution. Roasting is one of the most important steps in the electrolytic process, especially when leaching with dilute sulphuric acid, as the possible recovery is greatly dependent upon how well this step is performed. Several methods of preparing the concentrate, other than roasting, have been proposed. None of these is commercially feasible at the present time.

Production of Pure Zinc Solution.—Dilute sulphuric acid is the only solvent used in the leaching of roasted ore or concentrate for the commercial production of electrolytic zinc. Not only zinc but many other elements, if present in the roasted

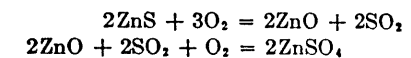
material, are dissolved by dilute sulphuric acid. Most of these elements must be removed from solution to ensure successful electrolysis. The production of a pure solution is really a combination of several steps: leaching to dissolve zinc, separation of solution and insoluble residue, purification of solution, and clarification of solution. This combination is of basic importance to the process as, given perfect roasting, the recovery of zinc is dependent on proper leaching and filtration, and the successful electrolysis of zinc sulphate solution is dependent on proper purification of solution.

Electrolysis of Solution.—The only successful commercial method so far developed for the production of metallic zinc from zinc sulphate solution is by electrolysis. Purity of solution is the essential factor. Probably no other process operating on such a large scale requires the same degree of purity. Other factors influencing electrolysis are the temperature of the electrolyte, current density, ratio of acid to zinc in the electrolyte, period of deposition, and purity of electrodes. Lead or lead-alloy anodes and aluminum cathodes are used. The current applied varies from 30 to 100 amp. per sq. ft. of cathode surface. Purified zinc sulphate solution is fed to the electrolyzing cells where, by the application of an electrical current, zinc is deposited as a metal on the cathode. For each unit of zinc deposited, approximately one and one-half units of acid are regenerated. The efficiency of this reaction decreases rapidly as the ratio of acid to zinc increases. For this reason no attempt is usually made to remove more than about 75 per cent of the zinc in solution. The spent electrolyte, containing about 25 per cent of the original zinc and the acid regenerated during electrolysis, is returned to the leaching division to be used for further leaching of roasted concentrates. The zinc deposited during electrolysis is removed at the end of regular periods and is melted and cast into slabs. *Recovery of acid*

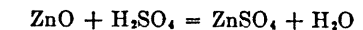
Zinc is electronegative to hydrogen, and it would be expected that zinc could not be deposited from an acidified solution of zinc sulphate. The hydrogen overvoltage on zinc, however, is high enough so that zinc plates out in preference to hydrogen. Some hydrogen is always evolved, especially with the higher current densities.

The simple chemical reactions involved in the roasting, leaching, and electrolysis of zinc are as follows:

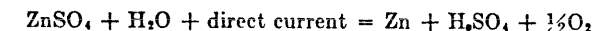
Roasting:



Leaching:



Electrolysis:



In addition to the divisions of the process as outlined, there might be added a fourth, treatment of the residue. The electrolytic-zinc process is particularly applicable to the treatment of the complex ores of the Western states, and there are in nearly every instance sufficient values in the residue to warrant their recovery.

The great variety of ores to which the process is applicable results in the production of several classes of residue. Each class of residue requires its own method of treatment to produce the greatest possible return. Lead smelting, copper smelting, wet methods, or a combination of methods, may be necessary depending on the class of residue produced.

PREPARATION OF CONCENTRATES FOR LEACHING

Roasting.—The main object of roasting for the electrolytic-zinc process is to obtain the maximum percentage of zinc that will be readily soluble in the leaching

solution. Zinc sulphide is practically insoluble in dilute sulphuric acid at ordinary temperatures. Zinc oxide is readily soluble in dilute sulphuric acid, and zinc sulphate is soluble in water. Roasting is done, therefore, to convert the zinc sulphide in the unroasted concentrate as completely as possible into zinc oxide and zinc sulphate. Only enough zinc sulphate to supply the acid requirements of the plant is normally desirable, as any excess must eventually be discarded. The acid requirements of a plant of this kind are usually small. The only acid losses are as insoluble sulphates and solution losses. The higher the lime and lead content of the concentrate, the greater will be the loss as insoluble sulphates. The chief loss of solution is as entrained moisture in the residue. Usually a zinc sulphate formation of 2 to 3 per cent sulphate sulphur in the calcine is sufficient to supply all acid losses. A greater amount of zinc sulphate than necessary tends to build up zinc and acid in the system. A higher concentration of zinc in the solution results in a greater loss of zinc in the residue and increases the difficulties of settlement and filtration.

Roasting Furnace.—Most electrolytic-zinc plants use some modification of the Wedge furnace for the roasting of zinc concentrates. The Wedge furnace is a circular multiple-hearth furnace of the McDougall type. Nearly every electrolytic-zinc plant using this furnace has developed some modification in design, until at the present time, as far as the electrolytic-zinc industry is concerned, there exists no standard form. Figure 1 shows the form of Wedge furnace from which these modifications were derived.

The type of Wedge furnace used by the Anaconda Copper Mining Co. at its Great Falls and Anaconda plants is 25 ft. in diameter. It has seven superimposed roasting hearths plus a top hearth for drying the feed. A 5-ft.-diameter hollow steel brick-lined revolving center shaft carries 26 cast-iron arms, four for each of the drier and first hearths, and three for each of the remaining six hearths. All the arms except those on the drier hearth are cooled with water delivered to the arms through a system of piping inside the center shaft. The center shaft is supported on a step bearing and, complete with bricks, arms, piping etc., weighs approximately 50 tons. The speed of the center shaft varies in individual furnaces from one revolution in 4 min. to one revolution in 2 min. The driving mechanism consists of a set of reducing gears powered by a 15-hp. 555-r.p.m. electric motor. The furnaces are fired with natural gas, usually by two burners on the seventh or bottom hearth, spaced 180 deg. apart. When additional heat is desired in other parts of the furnace, portable burners are set up in the furnace doors.

The concentrate to be roasted is fed by an apron feeder driven from the revolving center shaft. It is discharged from the feeder onto the outer edge of the drier hearth and advanced across the hearth by means of rabblers or rakes fastened to the furnace arms. When the material reaches the inside of the drier hearth, it falls through holes to the next hearth below, the first roasting hearth. The rakes on the rabble arms of the hearth are set to move the material outward; when it reaches the outer edge of this hearth, it falls through drop holes onto the next hearth, and so on down through the furnace. The roasted material, commonly called calcine, is discharged from the seventh, or lowest, hearth into two steel hoppers provided as a temporary storage for calcine. These hoppers discharge into cars for removing the calcine.

The gases produced by the roasting process pass upward through the furnace countercurrent to the material being treated. From the first roasting hearth, the gases are passed into offtake flues that lead to the main gas flue. The roasting of flotation or fine table concentrates in this type of furnace is productive of a large amount of flue dust which must be collected and returned to the furnaces for further treatment. A part of the dust settles out in the flues adjacent to the furnaces. These flues are hopped to facilitate removal of this dust, which is ordinarily returned to

the furnace where it was produced. A large portion of the dust, however, is collected very efficiently by a Cottrell precipitator and is fed to a furnace operating on flue

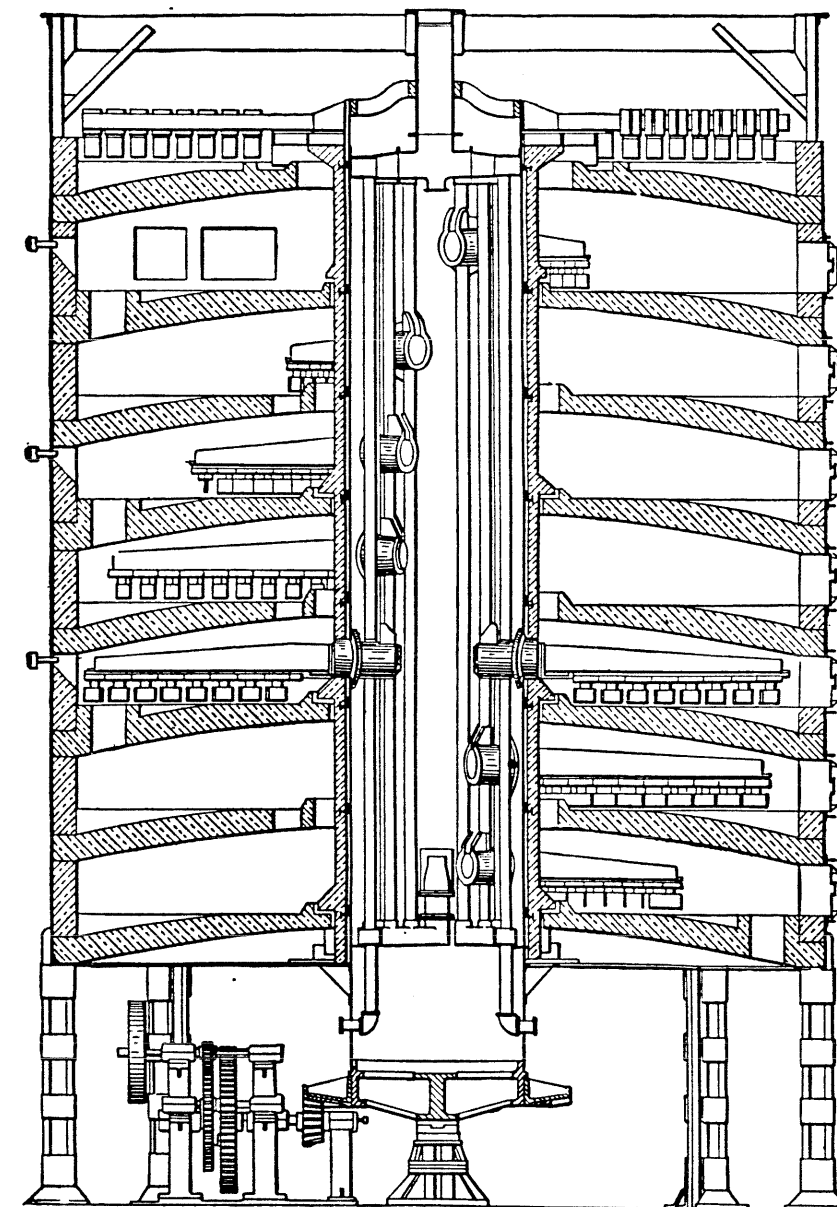


FIG. 1.—Wedge furnace.

dust alone. This method of handling the flue dust is much more satisfactory than attempting to treat a proportional amount of dust through each individual furnace.

The materials to be treated are flotation or fine table concentrates, over 50 per cent of which will pass a 200-mesh screen. The calcine product from the roasting furnaces contains a certain amount of oversize material that is screened out, crushed, ground, and returned to the furnaces for further treatment. Dust collected from the furnace flues is also re-treated through the furnaces. These last two materials contain an appreciable amount of unroasted matter which must be further oxidized before they are suitable for leaching purposes.

The amount of flue dust carried away from a furnace during roasting depends in large part on the fineness of the concentrate and on the volume and velocity of the flue gases. The amount of dust that can be carried by a gas of given volume depends mainly on the velocity of the gas stream. A reduction in velocity of a given volume results in an even greater reduction in the maximum load of dust that can be carried by that given volume of gas. In order to keep down the amount of flue dust produced by the furnace, it is necessary to keep the gas volume and velocity as low as possible by carefully regulating the door openings on each hearth to give only the amount of air necessary for roasting and for cooling the upper hearths. Ordinarily the Wedge furnace has but two gas offtake flues. The addition of one or more offtakes lowers the velocity of the gases very materially and allows more air to be admitted to the furnace without increasing the amount of flue dust produced. If a large portion of the dust collected from the flues is returned to one furnace (or more if necessary) and the gas volume on this furnace is held as low as possible, the amount of dust recirculated may be kept at a minimum.

The capacity of this type of furnace varies widely with the class of material treated. The amount of lead contained in the concentrate has a large effect on the amount that can be treated. The capacity of a furnace is greater for high-zinc concentrate containing relatively low lead values than for a lower grade high-lead concentrate. The limiting factor for low-zinc complex concentrates is the ability to cool the upper hearths without undue production of flue dust. In general, the higher the zinc content of the concentrate, the higher the roasting temperature required. The normal limits when roasting a high-grade zinc concentrate are 40 to 60 tons of new feed per 24 hr.

Lump coal, pulverized coal, oil, and gas have all been used as fuel in these furnaces. Gas is by far the most satisfactory. A large part of the ash from pulverized coal settles in the furnace and flue system and eventually finds its way out in the calcine. Then it adds to all subsequent operating costs, such as leaching, filtration, and residue treatment. Fuel requirements vary with the class of concentrate being roasted. When using pulverized coal containing a heat value of 10,000 B.t.u., the observed limits are from 7 to 18 per cent of the weight of concentrate. Oil requirements are about 20 per cent less than coal on a heat-unit basis of comparison. Gas requirements vary from 2500 to 3500 cu. ft. of 1000 B.t.u. gas per ton of concentrate.

The electrolytic-zinc plant of the Consolidated Mining and Smelting Co. of Canada, at Trail, B. C., has developed a "burning concentrate process" of roasting zinc concentrates. This method, also known as "flash roasting," under some conditions has decided advantages over the conventional method. The original roasting practice at Trail employed standard Wedge furnaces. Eight of these furnaces were converted to flash roasting by removing the second, third, fourth, and fifth hearths from each furnace to form a combustion chamber.

The top or drier hearth is covered and, along with the regular first hearth, is used to dry completely the wet concentrate feed. Some gas from the combustion chamber is by-passed through this chamber to aid in the drying process. The wet concentrate is fed at a controlled rate to the drier hearth through a closed chute. After being thoroughly dried while passing over the two drier hearths, the material is then delivered

Roast
Coal,
Fuel oil,
& Gas

First
Vertical
Flash
Furnace

to a ball mill situated near the furnace. The ball mill pulverizes all lumps formed during the drying process. The discharge from the ball mill is then elevated to storage hoppers over each furnace.

The material at this point is fine, dry, and at about 95°C. It is fed from the storage hoppers by air injectors which deliver it to the burner. At the burner it is mixed with air supplied by a fan and is blown into the top of the combustion chamber of the furnace. The material ignites immediately upon entering the furnace, and in burning maintains a temperature between 900 and 950°C. in the combustion chamber. No external heat is needed to maintain the roasting temperature, as all heat is supplied by the burning concentrate itself. The temperature of the combustion chamber is maintained between very close limits by carefully controlling the ratio of concentrate to air.

About 40 per cent of the material introduced into the combustion chamber is carried out of the furnace with the flue gases. The hot dust and flue gases pass through waste-heat boilers where approximately 1.1 lb. of steam is generated for each pound of concentrate treated. The gases pass from the boilers into cyclone collectors where most of the dust is removed. The remaining dust is then removed by passing the gas stream through a Cottrell precipitator.

The material settling to the bottom of the combustion chamber of the furnace, comprising about 60 per cent of the total, is rabbled across two collecting hearths at the bottom of the furnace. There the remaining sulphide is oxidized, and the finished calcine is then carried to a calcine storage by means of conveyers. The collecting chamber can, if necessary, be used as a sulphating chamber by the introduction of a strong atmosphere of sulphur dioxide. Under normal operating conditions, the calcine from the flash-roasting furnaces at Trail assays, on the average, about 0.3 per cent sulphide sulphur and 0.4 per cent sulphate sulphur.

The capacities of the suspension-type roasters at Trail have been increased by the introduction of oxygen into the furnace during roasting. The oxygen is obtained as a by-product from an ammonia plant.

The zinc roasters of the Giesche Spolka Akeyzna, Poland, have been changed over to suspension roasting. No heat recovery has been attempted, and the roaster gases are taken off the top of the furnace. It was found necessary to grind the flotation concentrates to obtain thorough roasting.

The advantages of this method of roasting are: more than doubling the furnace capacity, saving in cost of fuel, and production of gas rich enough in sulphur dioxide or acid manufacture. The disadvantages are: production of a much greater percentage of flue dust, higher gas temperatures, and the drying and grinding of concentrate.

The advantages outweigh the disadvantages heavily where fuel is expensive and acid is to be produced from the flue gases. Also, where large quantities of steam can be utilized, the waste-heat boilers are a decided advantage. By proper control of the air supplied to the furnace, fusion of the roasted particles is avoided and the resulting calcine can be leached without difficulty.

The Flin Flon plant of the Hudson Bay Mining and Smelting Co. uses modified Wedge-type roasters operating on the "split-draft" process. This type of furnace is equipped with gas offtake flues on both the first and seventh hearths. Under normal operating conditions, the draft splits at the third or fourth hearth, with about one-fourth the gas leaving the furnace from the first hearth. By regulating the amount of gas drawn from the upper or lower offtakes, the location of the heat zone in the furnace can be controlled. The amount of concentrate fed to the furnace is so regulated that the heat of combustion of the concentrate is enough to maintain roasting temperature. While no external heat is used for normal operation, several stand-by

ore
Cons.
inject
thru
burne
Cons
suppli
Heat
Energy
Cottrell
Precip
40%
Flue
dischar
60%
Bottom
oxygen
inject

burners using pulverized coal are installed on each furnace to be used in case of necessity and for heating the furnaces when starting up after a shutdown period.

The electrolytic plants at Ordzhonikidze and Cheliabinsk, U.S.S.R., each have six 25-ft.-diameter roasters designed to operate on the split-draft principle. The split-draft process permits the heat of combustion to be used under full control and elimi-

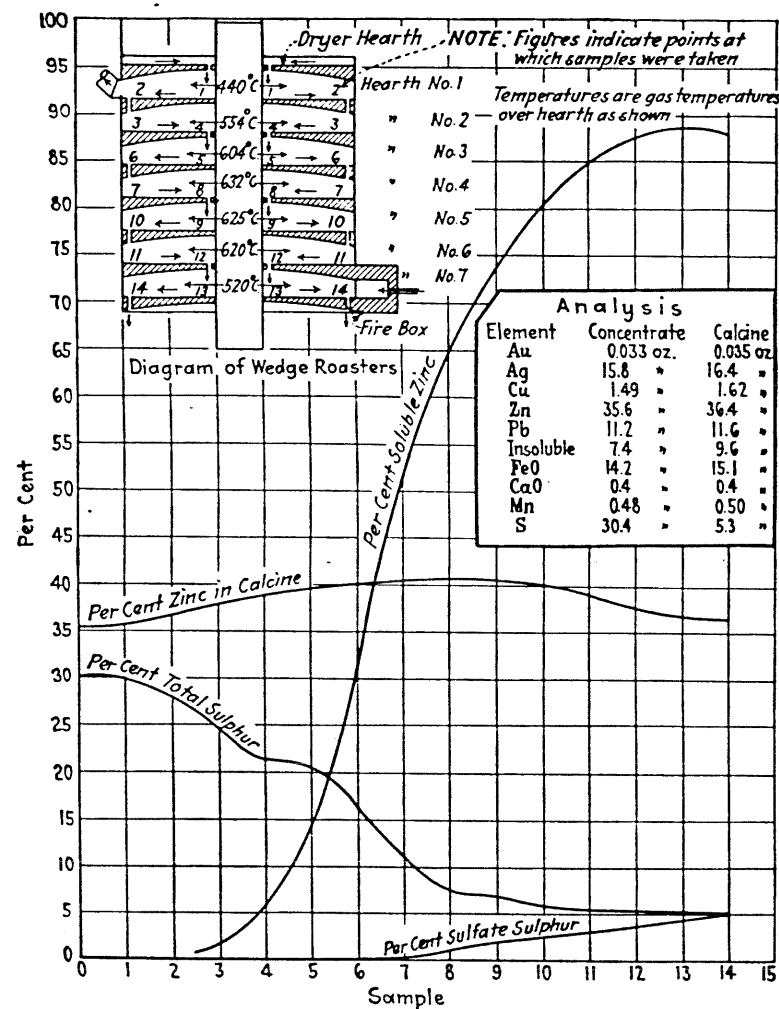


Fig. 2.—Roasting low-grade concentrates without returning flue dust.

nates the use of extraneous fuel. It permits a close control of sulphation, gives consistent low operating temperatures with a low ferrite formation, and increases the life of the roaster bricks and rabble arms.

The Electrolytic Zinc Co. of Australasia, at Risdon, Tasmania, has a somewhat different roasting practice from most other zinc plants. The material delivered to the Risdon plant is not raw concentrate but has been pre-roasted before shipment. This material when delivered contains about 7 per cent sulphur with about 6 per cent

as sulphides. It is wetted before shipment with water relatively high in chlorine and, being carried by ships, is also liable to accidental wetting with sea water.

The furnaces are of Risdon design and are a modification of the Leggo furnace used for roasting arsenical pyrites. Each furnace has four superimposed hearths 85 × 8 ft. Each hearth has a flue connecting to the main flue system. The furnace charge is fed on to the top hearth through a hole in the top, and from this hearth to the lower hearths through regulated openings. Each hearth is practically a separate furnace. The furnace is built on a slope of 1:12 and has 16 columns which carry the rabble arms for each hearth. The sweep of each rabble arm overlaps the sweep of the next in line, and by this means the material is carried the length of the furnace. Each furnace treats about 90 tons of charge per day, with a fuel consumption of 10 to 12 per cent of the weight of the charge. The fuel used in the furnaces is slack coal burned on a traveling-grate stoker.

The Formation of Ferrites.—The presence of iron in zinc sulphide ores causes the greatest loss in the electrolytic-zinc process. Under certain conditions, zinc oxide and iron oxide combine to form zinc ferrite, $ZnO \cdot Fe_2O_3$, which is insoluble in warm dilute sulphuric acid. No successful commercial method has yet been developed to prevent the formation of some zinc ferrite during roasting, but its formation can be partially controlled by a careful regulation of roasting conditions. The formation of ferrites is dependent on the iron content of the concentrate, the association of the zinc and iron content, the temperature of roasting, and the length of the roasting period. Analysis of the concentrate will not alone serve as a means of predicting the amount of ferrite that will be formed. A concentrate with a relatively low iron content, with the zinc and iron closely associated, will tend to form more ferrites during roasting than a concentrate with a higher iron content, but with the iron and zinc in less intimate contact.

Iron sulphide oxidizes at lower temperatures than zinc sulphide, and it is possible by careful control to make a preferential roast if the initial roasting temperature is kept below 600°C. The object is to prevent the simultaneous oxidation of iron and zinc as much as possible. Some zinc sulphide will always be roasted, however, even at low temperatures, with the subsequent formation of ferrites. If, however, the main bulk of the iron sulphide is roasted first, and the zinc sulphide later, the chances of combination are greatly reduced. When the particles of zinc and iron are very intimately mixed, as in marmatite, preferential or selective roasting is practically impossible and a high percentage of ferrite is bound to result. The general practice is to keep the temperature as low as possible throughout the furnace and, especially, to keep the temperature on the first two or three roasting hearths below 600°C. As the iron content of a concentrate increases, the possibility of making a selective roast also increases. Most low-iron concentrates roast with complete combination of the iron and zinc as ferrite. Figure 2 gives data taken from roasting low-zinc high-iron concentrate. The data in Table 1 were obtained in the laboratory on samples from the same class of concentrate and show that the analysis cannot be depended upon to determine the amount of ferrite formation.

Roasting Temperature.—Roasting depends almost entirely on the control of temperature and time. The length of the roasting period is set by the roaster speed and the design and position of the rakes on the rabble arms. While it is possible to change the speed of a furnace by a change of gearing, the speed is usually constant over long periods of time. A variation in rabbling time by a change in design and spacing of rakes is also possible but, like the turning speed of the furnace, has no flexibility of control. Therefore, the control of roasting is dependent on temperature, which is, in turn, controlled by the amount of fuel burned and the quantity of air admitted to the furnace.

Fe
cause
of
loss

Temp.
control
Necessary

TABLE 1

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO ₄	Per cent soluble Zn	Per cent As	Per cent Sb
Concentrate A.....	39.6	13.8	6.6	29.2	0.10	0.04
Calcine A.....	37.8	6.3	8.8	8.5	92.6	0.08	0.03
Concentrate B.....	47.3	3.4	7.0	32.2	0.53	0.17
Calcine B.....	44.8	6.6	8.5	8.1	94.2	0.23	0.05
Concentrate C.....	34.9	13.6	11.6	32.0	0.11	0.03
Calcine C.....	36.8	11.8	5.4	5.2	92.7	0.09	0.03
Concentrate D.....	34.3	17.8	7.5	28.4	0.08	0.03
Calcine D.....	33.8	7.4	6.0	5.9	89.1	0.07	0.03
Concentrate E.....	30.8	3.6	16.4	35.3	0.90	0.19
Calcine E.....	30.4	16.0	8.5	8.5	87.2	0.24	0.11

NOTE.—Roasts made at low temperature—650°C. maximum—with no attempt to control sulphate sulphur.

The maximum temperatures in roasting for the electrolytic-zinc process may be given as approximately 650°C. for complex low-zinc concentrates, and 750°C. for high-zinc concentrates. In order to obtain speed in roasting, the temperature must be carried as high as possible without materially lowering the solubility of the product.

TABLE 2

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO ₄ -S	Per cent soluble Zn
Concentrate A.....	32.3	8.2	15.6	32.4
Calcine A.....	35.0	3.8	3.2	80.3
Concentrate B.....	32.3	16.4	8.7	28.4
Calcine B.....	34.6	3.9	3.5	88.5

The initial temperature should be well under 600°C. for at least one roasting hearth. This is especially true for concentrates containing appreciable amounts of lead and iron sulphides. Lead sulphide fuses without roasting if the initial temperature is too high and forms a hard crust on the hearth under the rakes. It may also coat the particles of zinc sulphide and form lumps that will pass through the furnace without being roasted; these must be screened out of the calcine, crushed, ground, and returned to the furnace for additional roasting. As the initial temperature increases, the loss of lead through the formation of fume also increases rapidly. High initial tem-

peratures in the presence of iron sulphides are very conducive to the formation of zinc ferrites.

With the initial temperature low, the temperature lower down in the furnace must be increased to complete the roasting of zinc sulphide and to prevent the formation of an excessive amount of zinc sulphate. This temperature must also be kept

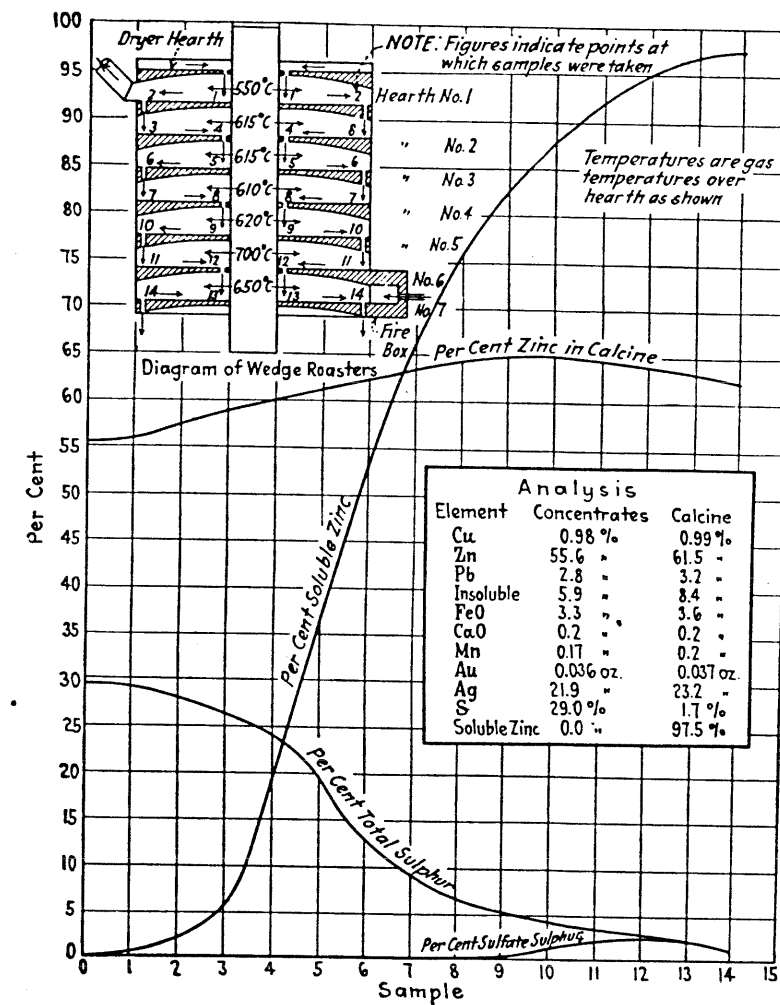


FIG. 3.—Roasting high-grade concentrates in Wedge furnace.

high enough to prevent any appreciable amount of sulphide sulphur being left in the calcine, as each unit of sulphide sulphur will hold approximately twice its weight of zinc as an insoluble compound. The temperature must not be raised too high, as an increase in temperature tends to increase the formation of zinc ferrites. Roasting then becomes a nice balance between the formation of ferrites and the amount of sulphide sulphur left in the ore.

Each concentrate treated is a problem in itself, and the best roasting conditions must be determined by actual practice. The best conditions for roasting a concentrate cannot be satisfactorily determined on a small scale, but must be tried under the actual roasting conditions in the furnace. Figures 2 and 3 give temperatures from the operation of two furnaces on widely different classes of concentrate.

TABLE 3

Hearth	Per cent SO ₂	Gas temperature, degrees Centigrade	Calcine temperature, degrees Centigrade	Per cent CO ₂
1	3.0	438	459	2.5
2	2.8	560	551	2.5
3	2.2	626	665	2.7
4	1.2	650	665	2.8
5	0.5	622	638	3.4
6	0.3	622	652	3.6
7	0.1	543	602	3.0

Temperature regulation in the furnace is obtained by varying the amount of air admitted into the furnace at different points, and also by varying the amount of fuel burned. The Wedge roaster radiates only a small amount of the total heat involved in the process. Some heat is conducted away by the cooling water in the arms, but is only a small part of the total. Approximately 80 per cent of the heat evolved during the combustion of zinc sulphide escapes with the flue gases. With the same zinc content, but with varying amounts of lead sulphide and iron sulphide, very different heat problems will be presented. Analysis of two concentrates and the resulting calcines taken from monthly averages in actual practice are given in Table 2. The difference of 4 per cent in sulphur content of these concentrates is due to the difference in iron content, and must be eliminated on the upper hearths, requiring more cooling air for concentrate A. If the lower part of the furnace is required to do too much roasting, the larger volume of hot gases from the lower hearths tends to raise the temperature on the upper hearths and will require more cooling air on these hearths. Too much air admitted to the hearths where sulphur is burning tends to raise the temperature still further. It is essential to keep the volume of gas as low as possible on the lower hearths if proper control of upper-hearth temperature is to be obtained without too great a total gas volume. Table 3 gives the temperatures and SO₂ analysis, by volume, of the gas on the different hearths of a furnace roasting low-zinc concentrate with excellent results. Pulverized coal was used for fuel.

Sulphate Roasting.—The term "sulphate roasting" as commonly used in connection with roasting for the production of electrolytic zinc is really a misnomer. It is not desirable to form more zinc sulphate than is required to offset the loss of acid in the leaching plant. This term was coined to apply to the set of roasting conditions necessary to supply acid for a plant using limestone or milk of lime for neutralization in the leaching division, thereby greatly increasing the loss as insoluble sulphates in the residue. In this process, unless sufficient acid was formed to offset this loss, it was necessary to add fresh acid to the system. The maximum amount of sulphate sulphur formed in practice was about 6 per cent of the weight of calcine. Ordinary

roasting practice on the same class of material would give about 3 per cent sulphate sulphur.

The chemical reactions involved in the formation of sulphate sulphur are debatable, as are all the reactions during the roasting process. In any case they are many and involved.

The reaction $ZnS + 2O_2 = ZnSO_4$ is possible, but if occurring where the temperature is high, it would immediately be broken down into zinc oxide with the formation of SO₂. Whether zinc sulphate is formed according to the reaction $ZnO + SO_2 = ZnSO_4$ or by $ZnO + SO_2 + O = ZnSO_4$ is not especially important. In either case the presence of iron as a catalyst is necessary to the reaction. Some ferrite, ZnO-Fe₂O₃, may also be decomposed, forming ZnSO₄, in the presence of a strong atmosphere of SO₂.

A furnace roasting for a certain amount of zinc sulphate in the calcine must be operated at a lower temperature, especially on the lower hearths, than when roasting in the normal manner. A large amount of air must be admitted to the lower hearths, which gives a greater dust loss due to the increased gas volume.

Behavior of Impurities in Roasting.—Varying percentages of arsenic and antimony are eliminated in roasting zinc concentrates, as is illustrated in Table 1. The amount eliminated probably depends on the form in which they occur in the concentrate. Most zinc ores are quite low in these impurities, which is indeed fortunate as they are among the most detrimental to the process.

Some copper combines with iron during roasting, the combination being insoluble in dilute sulphuric acid. Concentrates containing high percentages of iron produce a smaller proportion of soluble copper than those low in iron. Some copper sulphate is formed on the upper hearths of the furnace, but is later decomposed by the higher temperature on the lower hearths. *cu combi with Fe*

A large percentage of the lead content of the concentrate may be volatilized if the temperature of the upper hearths is too high. Too high a temperature in the furnace also may cause the lead to fuse and coat a considerable portion of the unroasted zinc sulphide, preventing further roasting of the coated particle. Some of the fused lead may also work into the hearth bed, forming a hard crust.

One disadvantage of the sulphate roast is the high percentage of soluble iron in the calcine. This would indicate that some iron sulphate is formed in roasting. In roasting without the necessity of forming sulphates, the finishing temperature is high enough to break up the iron sulphate, and most of the iron in the calcine is then insoluble in the leaching solution. All iron that is dissolved in the leaching solution is finally precipitated from solution as ferric hydrate or basic sulphate and, when too much is present, will render the residue from the leaching plant practically impervious to the passage of wash water.

Silver is rendered less soluble at low than at high temperatures; but when the initial roasting temperature is high, the silver is apt to be volatilized. *Ag volatilize*

Chlorine and fluorine, if present, are largely eliminated during roasting, as most chlorides and fluorides are volatile at the temperature of roasting.

Notes on Roasting.—The bedding of calcine between the rakes and the brick hearths is found to contain a high percentage of zinc sulphate, especially on the second, third, and fourth hearths. This material becomes quite hard; the hardness increases with the temperature of roasting. At frequent intervals the rakes are removed from a rabble arm, a plow is put on, and the crust is cut loose from the hearth. This crust is then removed through the furnace doors. If allowed to stand in the open, this crust will absorb moisture and disintegrate. Usually this crust is crushed, ground, and returned to the furnace to be given additional roasting. In order to prevent the formation of heavy crusts, a layer of sand is spread over the brickwork

of the hearth before the furnace is started. This sand is renewed at intervals of about two years thereafter.

Some lumps are always formed during roasting and should be removed from the calcine before delivery to the leaching plant. If Pachuca tanks are to be used for leaching, the calcine must be screened through $\frac{1}{8}$ -in. screens. The oversize product usually contains enough sulphide sulphur to cause trouble in leaching, especially in cases where high acid strengths are used. When sulphide sulphur is present, a reduction of iron in solution from the ferric to ferrous state may take place with an increase in the loss of zinc in the residue. The oversize material screened from the calcine is crushed, ground, and returned to the furnace for further treatment.

The hot calcine from the roasters must be cooled in order to prevent injury to employees and to lessen the hazards from fire. In the Anaconda plants the processes of cooling and screening are carried out together. The hot calcine from the roasting furnace is conveyed by larry cars to bins above the coolers. These coolers are horizontal rotating cylinders, lined with a large number of pipes. Cooling water is circulated through the pipes; and the calcine is cooled during passage through the cylinders. The calcine when reaching the discharge end of each cooler is passed over a $\frac{1}{8}$ -in. trommel screen rotated by the cooler. The undersize material drops through the screen into storage bins directly beneath. The oversize falls into a screen conveyor where it is carried to a vibrating screen where further classification is made. The large lumps that will not pass through a $\frac{3}{8}$ -in. screen are collected, crushed, ground in a ball mill, and returned to the roasters. The lumps that pass a $\frac{3}{8}$ -in. screen but not a $\frac{1}{8}$ -in. screen are ground in a ball mill, without crushing, and also returned to the roasters. The material passing through the $\frac{1}{8}$ -in. screen is regular calcine and is suitable for delivery to the leaching plant.

PRODUCTION OF A PURE ZINC SOLUTION

Classification of Operations.—The operations necessary for the production of a pure zinc solution from roasted zinc concentrates fall into two main types: leaching and purification. Theoretically, leaching should be concerned only with the dissolving of zinc oxide and sulphate; but, from the economic standpoint, it must also include the treatment of zinc ferrites and other difficultly soluble compounds. A leaching process strenuous enough to dissolve certain zinc compounds may take other elements into solution, thus making the purification process much more complicated. The purification processes, under these conditions, fall into three main classifications: ferric hydroxide purifications, zinc-dust precipitations, and special chemical purifications.

Chemically, the leaching and purifying processes are separate and distinct, but in commercial practice they are sometimes so interwoven that division is difficult. Much of the actual purification of solution takes place in the leaching tanks. The dissolving of zinc oxide, for example, is often simultaneous with the removal of certain impurities by ferric hydroxide in a single neutral leach.

Equipment.—Standard types of leaching, settling, filtration, and clarification equipment have been adapted to the needs of the process, thereby simplifying the mechanical problems. Pachuca tanks are generally used for leaching, the size depending on the needs of the plant; standard thickeners are used for thickening of pulp; standard continuous vacuum filters are employed for filtration of the thickened pulp; any type of mechanical agitator of large capacity will answer for zinc-dust purification; and standard pressure filters are used for clarification of solution. All equipment should be constructed of materials not attacked by acid or by copper in solution. Lead and wood are commonly used for the construction of parts in contact with acid, and lead, copper, or bronze for parts in contact with neutral solutions containing copper. The recent developments in alloys have produced materials that are rapidly

being adopted by the electrolytic-zinc industry. A further increase in the use of these materials can be expected as their production is increased and their applications are proved.

The use of materials that are resistant to corrosion requires considerable extra capital outlay over the cost of similar equipment of iron and steel. This is largely offset by the high salvage or scrap value that can be credited against the heavy first cost of construction.

The Pachuca tank is especially well adapted to the continuous leaching practice that has been adopted by the larger plants. The Pachuca tank operates on the same principle as the common air lift. Pulp is circulated and agitated by means of an air lift placed centrally in the tank, the pulp entering the lift at the bottom of the tank and being discharged at the top. The common size of tank is 8 to 10 ft. in diameter and 20 to 30 ft. deep. An inverted cone built into the bottom of the tank serves to deflect solid particles to the center so that they will be drawn into the air lift. The tank and air lift are made of wood, and the tank staves are bound together with iron hoops covered with sheet lead. An extra lining of wood inside the tank serves as a protection to the tank staves and can be easily renewed when necessary. This adds materially to the over-all life of the tank proper. Figure 4 shows the usual form of a Pachuca tank, with the method of supporting the central air lift and of admitting the air to the lift.

Compressed air at 20 to 30 lb. pressure is employed for agitation of the pulp. The consumption of air ranges from 100 to 150 cu. ft. of free air per tank per minute in order to maintain sufficiently violent agitation to prevent classification of the pulp. Even then some classification takes place, and over a long period of time the tank begins to build up in solid particles too heavy to be moved by normal agitation. It is advisable that the air supply to the tanks be also connected to a source of air under 80 to 90 lb. pressure. Then, when a tank begins to load up in the bottom with heavy material, a short period of more violent agitation will usually clear it.

The tanks in continuous-leaching practice are in series with connecting launders at the top of the tanks. The rate of flow through the series of tanks may be regulated by partially closing the connections between tanks. The number of tanks in series depends on the volume of pulp to be handled per unit of time and the length of time required to complete the reactions.

The leached pulp going to the neutral thickeners sometimes contains such a large amount of coarse material or "sand" that, unless removed, it would cause trouble with the thickener mechanism. If this is the case, the pulp is first passed through some type of classifier or sand trap and the coarse particles are removed. The trapped "sand" is then either added to the thickener underflow or given special treatment.

Standard thickeners are used for the separation of solution and solids. These are much the same type as those used in cyanide practice; but more slope and a larger discharge cone for the thickened pulp should be provided, especially for thickeners handling an acid product. The tanks are made of wood staves held together with iron hoops covered with sheet lead. The bottoms of the thickeners are often made of concrete poured over sand on a wooden floor. Overflow launders are made of wood. They may be lined either with brick or with a thin layer of wood that can be easily replaced when worn. Launders for use with acid-bearing solutions are often lined with sheet lead.

The drums or forms of the continuous vacuum filters used are made of wood or bronze, and the tanks are of either wood or steel with a lead lining. All pipes and fittings are of copper or bronze. For the filtration of a slightly acid pulp, the best filter cover yet developed is a pure unwashed wool blanket, placed so that the nap is on the outside of the filter. Such a cover will not "blind" easily, as the threads do

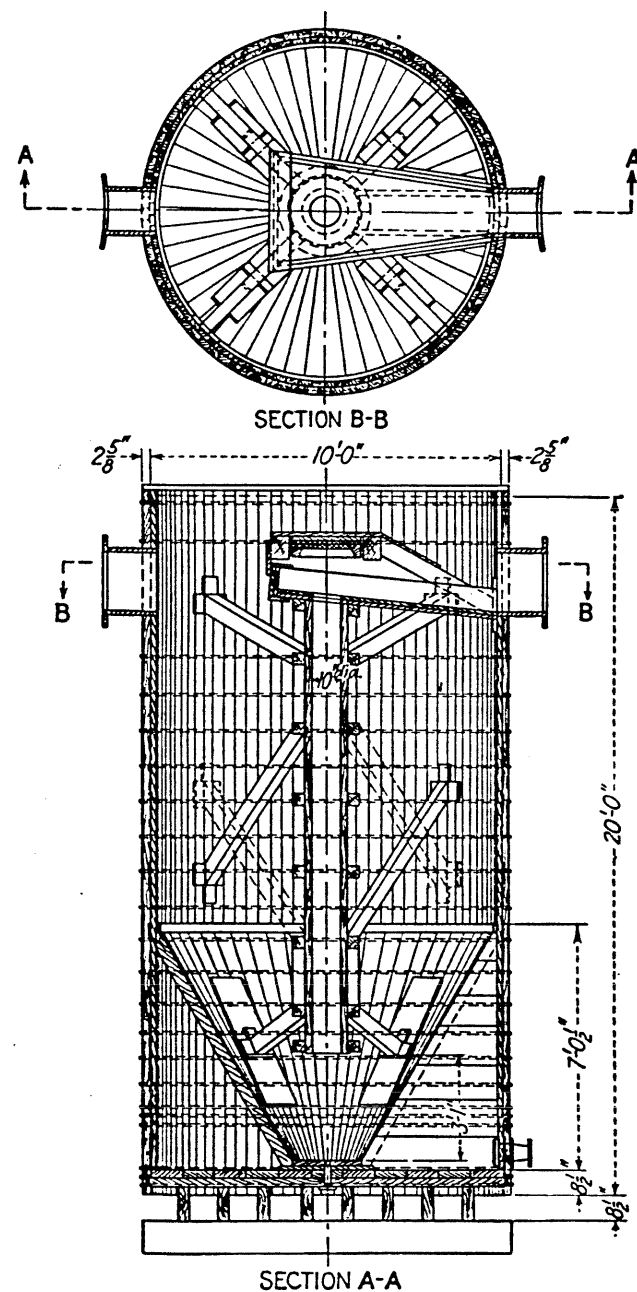


FIG. 4.—Pachuca tank for zinc leaching.

not swell when soaked in dilute acid. Also the nap acts as an automatic valve, closing when under suction and opening and freeing the cloth when under pressure. The natural oil in the wool protects the fiber against attack of dilute sulphuric acid. The dry vacuum system is used, and the solution receiver is made of either wood or bronze. To prevent vapor or spray from getting into the vacuum pumps and corroding valves and cylinders, receivers and traps should be of extra-large capacity.

Mechanical agitators with bronze or wood shafts and impellers are used for zinc-dust purification of solution. Plate-and-frame filter presses of bronze are generally used for clarifying the solution. Zinc sulphate solution, even when free of copper, will cause iron plates to corrode quickly, thereby plugging solution passages. All pumps and solution lines for handling neutral solutions containing any copper are made of bronze, copper, or stainless steel. Lead or stainless steel pumps are used for acid solutions, while wood or lead lines are used for conveying the solution.

Leaching.—The primary object of leaching is to dissolve all zinc oxide and zinc sulphate contained in the roasted concentrate in dilute sulphuric acid according to the reaction of $ZnO + H_2SO_4 = ZnSO_4 + H_2O$. Unfortunately, some iron, arsenic, antimony, silica, alumina, copper, cadmium, cobalt, germanium, and a few other elements are also dissolved and must be removed from solution before successful electrolysis can be carried out. It is necessary to neutralize completely all sulphuric acid to ensure the removal of most of these impurities. This may be done as a continuation of the leaching operation by the addition of finely ground limestone or milk of lime. This constitutes what is known as "single" leaching. It is not possible to neutralize exactly all free sulphuric acid and precipitate the necessary impurities by the addition of calcine. Excess calcine is required to complete the reactions, resulting in a serious loss of zinc in the residue and undissolved zinc oxide. In order to allow the use of calcine for neutralization and precipitation of impurities, without impairment of zinc recovery, a leaching system is employed whereby the residue from the first or neutralizing leach is treated with an excess of dilute sulphuric acid to dissolve all acid-soluble zinc. This system of leaching is known as "double" leaching.

"Single" leaching may be conducted as either a continuous or intermittent operation, but is more easily controlled if the intermittent or "batch" system is used. Calcine is added to regenerated acid from the electrolyzing cells until the acid strength is reduced to as low a figure as possible without impairing the satisfactory recovery of zinc—0.3 to 0.5 per cent H_2SO_4 . Limestone, finely ground, or milk of lime is then added in sufficient amounts to neutralize the remaining acid. Enough excess must be added to precipitate all the iron, silica, alumina, arsenic, and antimony present and to coagulate the pulp so that good settlement of the residue and a clear thickener overflow is obtained. A great deal of care must be taken by the operator in the single leaching system in order to get a satisfactory extraction of zinc. Only enough calcine should be added to bring the acid strength down to the desired point after a long period of agitation, as any excess over this amount will result in a loss of zinc. Milk of lime and, to a less degree, limestone will precipitate zinc from a neutral zinc sulphate solution, causing some loss of zinc. All the acid neutralized by limestone or milk of lime must be replaced either by the addition of fresh acid or by increasing the amount of zinc sulphate formed during roasting. The calcium sulphate formed by the use of limestone or milk of lime increases the bulk and moisture content of the residue. These materials when used are also quite an additional expense in the supply account. Normally, the only justification for the use of single leaching with dilute sulphuric acid is the saving in the cost of plant and in the operating cost. Only a single set of tanks and thickeners, with the necessary auxiliary equipment such as classifiers, pumps, etc., is required for the application of this method of leaching. A plant producing only a small daily tonnage of zinc, requiring a small volume of solution,

elements are completely removed from solution. At least 10 units of iron for each unit of impurity is necessary for complete elimination.

The first leach is so controlled that a large excess of zinc oxide, over that necessary to neutralize the acid and to precipitate the iron, remains in the pulp. This hastens the precipitation of silica, alumina, iron, etc., and causes soluble silica to precipitate in a somewhat granular form. The pulp under these conditions settles readily in the thickeners. Heat also aids these reactions, and the higher the temperature, the more complete the purification of solution and the better the coagulation of the pulp. As this is usually the only purification step for arsenic and antimony, the leach must be so controlled that it is known positively at all times that this purification is complete. A simple method has been adopted for detecting the merest traces of arsenic and antimony in solution. A hydrogen generator using pure zinc and sulphuric acid is set up. The gas generated is passed through lead acetate solution to remove any traces of hydrogen sulphide, and then through silver nitrate solution. The solution to be tested is added to the hydrogen generator, and the silver nitrate solution is watched for a change in color. A trace of arsenic will give a brown discoloration and larger amounts will form a black precipitate.

Samples of the leach discharge are taken at regular intervals and tested for ferrous and total iron, arsenic and antimony, and copper. *Fe test* The test for iron is by titration with potassium permanganate, or it can be roughly determined with potassium sulphocyanate. The test is made by first adding a few drops of nitric acid to the sample to oxidize any ferrous iron present. Then the addition of a few drops of potassium sulphocyanate will indicate the amount of iron present by the depth of red color produced.

The recovery of zinc in the first, or neutral, leach is low, usually not over 60 per cent of the acid-soluble zinc being extracted. This is because of the large excess of zinc oxide necessary for complete precipitation of impurities. This necessitates the addition of about one-half of the spent electrolyte to the second, or acid, leach. If the neutral-thickener underflow product is not filtered ahead of the acid, a large quantity of neutral solution is recirculated through the system. This increases greatly the volume of acid-thickener overflow and dilutes the acid strength of the neutral leach to about one-third that of the spent electrolyte. This circulation of neutral solution has no particular disadvantage except for the number of acid thickeners and pumps required to handle the solution.

The object of the second, or acid, leach is to recover as much of the acid-soluble zinc as possible and the least quantity of impurities, as any impurities dissolved must be returned to the first leach. Spent electrolyte is added to the thickened or filtered neutral pulp in sufficient quantity to insure the presence of excess acid in the leach discharge. The amount of excess acid added largely determines the amount of impurities dissolved. If sufficient time is given for the leaching operation, practically all the acid-soluble zinc and only a small part of the total impurities will be leached with an acid strength of 0.5 per cent in the leach discharge. Figure 6 illustrates graphically the behavior of some of the soluble impurities in the first and second leaches. Some of the impurities dissolved in the second leach are derived from the excess calcine added in the first leach. If the acid strength is carried as high in the second leach as in the first leach, more impurities will be dissolved because there is much less zinc oxide present to neutralize the acid. If most of the zinc oxide is dissolved while there is still an appreciable amount of acid present in the leaching solution, the acid then has a greater opportunity to act on the more insoluble impurities. Until all iron, arsenic, antimony, etc., soluble in an acid solution of given strength is dissolved from the pulp, the acid-thickener overflow is a saturated solution of these impurities for that acid strength. With the volume of the solution constant, more or

less of these impurities will be dissolved if the acid strength is increased or decreased. An increased volume of solution at a given acid strength also increases the amount of impurities dissolved. Therefore, if either the volume or acid strength of acid-thickener overflow is increased, the amount of impurities circulated will increase up to the point where all these elements soluble in the existing acid strength have been dissolved. Also, if either or both the volume and acid strength is decreased, less impurities will be circulated. It is highly desirable to keep the volume of solution and the amount of impurities circulated at a minimum to facilitate settlement in both the neutral and acid thickeners. A decrease in the volume of solution circulated also slows down the flow of solution through the same amount of equipment and gives time for more complete leaching. A decrease in the volume of solution circulated can

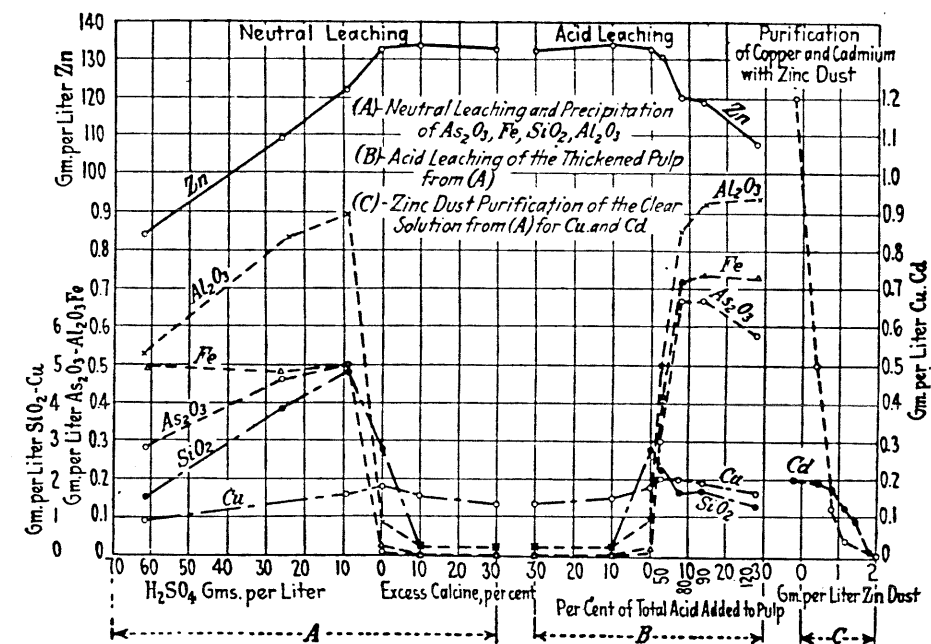


FIG. 6.—Behavior of soluble impurities.

best be accomplished by filtering the neutral-thickener spigot product ahead of the second leach. The filtered solution can then be added to the neutral-thickener overflow instead of circulating it through the leaching and settling system. Dissolving a larger amount of zinc in the first leach reduces the amount of solution required in the second leach, but carrying this too far is dangerous practice, as some excess zinc oxide is necessary for complete precipitation of impurities and for coagulation of the pulp.

The pulp from the acid leach does not settle as rapidly as properly coagulated neutral pulp. Some fine solid material always overflows the acid thickener and is put back into the neutral system. This constitutes an additional burden for this equipment. The amount circulated depends partly on the rate of flow through the thickeners. A reduction in the volume of solution passing through the acid system will, therefore, reduce the amount of solids as well as the amount of impurities returned to the neutral system.

An apparently simpler method of accomplishing the desired results from the double-leaching system would be to treat all the spent electrolyte with enough calcine to reduce the acid content of the leaching solution to about the same strength as the acid-thickener overflow—0.3 to 0.5 per cent H_2SO_4 —and then to neutralize and purify the resulting solution with excess calcine or limestone as a separate step. In this method, if calcine is used, the residue is returned to the leaching system, or if limestone is used, the residue is discarded. This method of leaching dissolves more impurities from the calcine because of the high acid strength of the leach. The residue from a leach of this type settles very slowly and is difficult to filter. Precipitated hydroxides and gelatinous silica require the weight of the main body of the residue to carry them down in the thickeners. They also filter much more readily when mixed with the sandy portion of the residue.

"Continuous" vs. "Batch" Leaching.—The continuous-leaching system is well adapted to plants handling a large volume of solution and having a fairly uniform feed. The main disadvantage of the continuous-leaching system is that sudden changes in the analyses of feed make a close control of the purification part of the leach almost impossible. It is therefore necessary that a continuous-leaching system be operated at all times under conditions suited to the maximum amount of impurities that might be encountered. This is the only positive way to ensure that no improperly purified solution will get by to the electrolyzing cells. With a batch-leaching system, each tank of solution can be held until its purity is assured. A larger proportion of the zinc content of the calcine can be recovered in the neutral leach with the batch system, as more time can be allowed for the addition of calcine and for agitation between additions. A much closer control can also be had of the amount of calcine added in excess of that necessary for neutralization. This results in less acid-thickener overflow returning to the neutral leach and improves conditions generally in the acid leach.

Air consumption is greater with the continuous-leaching system than with the batch system for a small plant. This is because it is necessary to maintain agitation in all the tanks continuously to prevent settling of the pulp, which would plug the air lifts. With the batch system each tank is completely emptied at the end of each leach, and air is used only during the actual period of leaching. A plant producing 50 tons of zinc per day, even with a low-acid process, will require less than 1000 tons of solution per 24 hr. This amount of solution can be handled more economically and with better leaching results in the same number of tanks operating independently than if arranged in series. As the volume of solution increases beyond the capacity, if operated independently, of the minimum number of tanks that can be placed in series for successful continuous leaching, then the comparison changes in favor of continuous leaching, owing to the saving in time required for filling and discharging.

Labor and repair charges are lower with continuous leaching, and the entire leaching operation is simplified. The capacity per tank is greater, giving fewer units for leaching and for calcine storage. Also, less difference in elevation is required between leaching tanks and thickeners, when gravity feed is used, owing to the fact that the tanks are discharged from the top instead of the bottom.

In general, plants of small capacity and those having a very variable feed are best served by the batch system, and those of large capacity and having uniform feed are best served by the continuous system for the neutral leach. For the acid leach the continuous system is preferable for all plants.

Purification of Neutral Solution.—Neutral-thickener overflow will be free of iron, arsenic, antimony, tin, bismuth, and silica, if the neutral leach has been properly carried out. The overflow will, however, contain 40 to 60 per cent of the copper and most of the cadmium originally present in the calcine. These two are usually the major impurities, but germanium, nickel, cobalt, etc., will also be found in the solution

if these elements were in the calcine to any extent. Some of these impurities have an adverse effect on ampere efficiency and must be removed to avoid trouble during electrolysis. Others are plated out with zinc and must be removed from solution previous to electrolysis if a pure zinc metal is desired. Both types of impurities are usually removed from neutral-thickener solution by mechanical agitation with finely divided zinc dust. The process of purification is usually so complex that adequate control cannot be obtained by continuous purification systems. Mechanical agitation is preferred to air agitation because of the tendency of certain impurities to oxidize and redissolve on contact with air. A single zinc-dust treatment will sometimes remove all undesirable impurities from solution, but often the purification must be divided into two or more "stages," each with its individual precipitation and filtration. An excess of zinc dust over the theoretical replacement amount is usually necessary to effect complete precipitation of impurities. Most of this excess zinc can be recovered from the purification residue and does not constitute a loss. The extent and intensity to which purification must be carried out, and the exact manner in which it is performed, depends on the particular impurities present, their relative amounts, and the degree of purity desired in the metal produced.

Copper and cadmium are the two harmful impurities usually found in relatively large amounts in the neutral-thickener overflow. If they are the only impurities present, both are easily removed by a purification with zinc dust. Copper precipitates first and has no tendency to go back into solution. Cadmium removal is not so complete; an excess of zinc dust above the theoretical replacement amount is necessary for adequate purification. The precipitation of cadmium is partially dependent on the copper content of the solution. A small amount of copper assists in cadmium removal; but if the ratio of copper to cadmium is high, the freshly precipitated cadmium tends to redissolve, and an even greater excess of zinc dust must be used.

Copper and cadmium are seldom the only harmful impurities found in neutral-thickener overflow. The presence of copper is beneficial in removing these other impurities, and if sufficient copper is present, most of them can be eliminated in the same zinc-dust purification that removes copper and cadmium. If not enough copper is originally present to make the purification sufficiently strenuous, it can be supplied by the addition of copper sulphate solution. The presence of other impurities and the addition of copper to remove them increase the tendency of cadmium to redissolve. In many instances the re-solution of cadmium is so great that a second zinc-dust purification must be made. This is especially true if high-grade zinc is to be produced. In this case the first treatment with zinc dust precipitates all the copper in solution, together with most of the cadmium and other impurities. The purification residue is filtered off, and more zinc dust is added to the clear solution. This second purification completes the removal of cadmium. It is sometimes made more effective by the addition of a small amount of dissolved copper, usually less than 0.1 g. per l.

Arsenic and antimony are often present in neutral-thickener overflow in small amounts, although, theoretically, the iron-hydroxide precipitation in the neutral leach should completely remove them from solution. The zinc-dust purification is very effective in removing these two impurities if enough copper is present.

Antimony may be present in some ores in sufficient quantities to complicate the usual neutral-leach purification. This condition is rarely met, but was encountered in the treatment of fume from the Mammoth smeltery at Kennet, Calif. Purification of solution in this case was accomplished by precipitating arsenic, antimony, copper, and cadmium with hydrogen sulphide gas. The neutral solution was acidified to 0.5 to 1.0 per cent acid and treated with H_2S gas. This method has received little favor from the industry for several reasons: it is difficult to remove the last traces of antimony in this manner within a reasonable length of time without the use of an

enormous amount of equipment, hydrogen sulphide is both obnoxious and poisonous and requires special care and equipment for application on a large scale, and settling and filtration of precipitated antimony are difficult, due to the extreme fineness of the particles.

Silica, if not removed from solution in the neutral leach, is precipitated by zinc dust. This increases the amount of zinc dust required and impairs subsequent filtration by "blinding" the filter medium. An excessive amount of silica tends to form a gelatinous coating around each particle of zinc dust; in extreme cases this action is so great as totally to prevent further purification. This condition requires special treatment to be given in the neutral leach to reduce the amount of silica in the neutral solution. Solids overflowing the neutral thickeners, because of poor settlement, will also raise the consumption of zinc dust and increase the burden on the clarification filters. In order to obtain the slightest efficiency from the zinc dust used, the solution to be purified must be free from mechanically held solids and from such soluble impurities as silica, ferric sulphate, and free acid. Ferric sulphate and free acid will dissolve precipitated cadmium and increase the consumption of zinc dust. Filtration of the neutral-thickener overflow is sometimes resorted to in order to obtain a solution absolutely free of solids.

The discharge from the purification tanks is either filtered direct in a pressure filter to remove the purification sludge, or is first sent to settling tanks to take some of the load of solids from the filters. While settling relieves some of the load, it also increases the possibility of cadmium becoming oxidized and "riding back." Filtration at this point must be perfect, and the filtered solution should be crystal clear. Any solids going through the filter medium are certain to cause trouble later in the electrolyzing cells. If the solid particles are copper or cadmium sludge, they will be dissolved by the acid in the cells and impair either the ampere efficiency or the quality of the metal produced, or both; if the solids are particles of residue overflowing the neutral thickeners, arsenic and antimony will be dissolved in the cells. Settling alone is not sufficient to ensure the necessary clarity of solution. The solids from the purification step are treated in a separate leaching cycle for the recovery of zinc, copper, and cadmium.

Filtration of Residue.—The most serious problem in the filtration of residue is to avoid the loss of zinc as entrained solution in the final material. Pulp that is slightly acid is especially difficult to handle. The gelatinous precipitates of iron and aluminum hydroxide and silica form a cake more or less impervious to the passage of wash water. The residue from a low-grade concentrate contains a rather high proportion of sandy material and can be washed with sprays. As the zinc content of the concentrate increases, the proportion of gelatinous to sandy material increases and washing becomes more and more difficult. Finally a point is reached where sprays cannot be used satisfactorily and washing must be done by dilution. A normal residue filter cake from a concentrate containing 30 to 35 per cent zinc will contain about 25 per cent moisture, while a residue from a concentrate containing 55 per cent zinc will carry 35 per cent moisture or more.

Washing by replacement is more efficient, less expensive, and requires less water than washing by dilution. In either type of washing, hot water is more efficient than cold. The viscosity of zinc sulphate solution increases with a decrease in temperature, and as the viscosity increases, it is less readily miscible with water. Heating the pulp to be filtered increases the capacity of a filter owing to freer passage of solution and also decreases the moisture content of the filter cake. The amount and method of washing are partly governed by the zinc content of the solution in the pulp being filtered. As the zinc content of the solution increases, the loss of water-soluble zinc increases, unless additional washing is provided.

A combination of washing and replacement and dilution is generally used when treating a residue from low-grade concentrates. Spray washing is used first, the resulting cake is repulped with hot water in a suitable agitator, and the resulting pulp is refiltered on a second filter on which spray washing is used. Repulping may be done in several types of agitators, but an adaption of a pugmill is one of the simplest and cheapest devices. A trough is fastened to the cake-discharge side of the filter to receive the cake as discharged. In this trough is a revolving shaft carrying pugmill blades and driven from the filter mechanism. Water is added to the trough in sufficient quantity to form a pulp of the proper density and after being mixed with the cake is discharged to a second filter. The amount of wash water that can be used is limited by the moisture carried out in the residue and the evaporation throughout the plant, unless some solution is discarded for other reasons. Pulp fed to the filters should be sufficiently thick to prevent much classification in the filter tank, or the sandy material will settle in the tank, and the filter cloth will become "blinded" with slime.

Washing a residue produced by high-grade concentrates presents a somewhat different problem. Here the pulp contains a relatively low percentage of sandy material, and washing with sprays is not practical. Repulping this residue results in a frothy sticky mass which is difficult to filter and retains a large amount of moisture. Even handling this pulp through a centrifugal pump increases its resistance to filtration. This pulp is usually handled in some type of filter, such as a Moore filter, in which washing is done by replacement. This step is then followed by a second filtration in which the pulp is dewatered as much as possible.

Vacuum used should be maintained as high as possible in order to reduce the moisture in the cake to a minimum and to keep the capacity of the filter at a maximum. The dry-vacuum system is much to be preferred, but must be provided with large solution receivers and moisture traps to avoid carrying solution or spray into the vacuum pumps. A slight leakage of solution or spray will soon corrode the valves and cylinders of the pumps to a point where they lose efficiency and will in a short time cause more serious trouble through breaking of valves and pistons. Traps and receivers made of wood staves are preferable to steel tanks with lead linings. Lead linings tend to collapse and break along the seams, giving the solution a chance to corrode the tank shell, and for this reason are expensive to maintain. Bronze or copper may be used in many cases but are expensive to install.

Recovery of Zinc from Residue.—The residue from the treatment of any concentrate containing iron will contain some undissolved zinc in the form of zinc ferrite. The residue will also contain any unroasted zinc sulphide introduced with the calcine, some zinc sulphate as entrained solution, and some undissolved zinc oxide in the small lumps that have not been penetrated by the leaching solution. As a general rule, the higher the zinc content of the concentrate, the smaller the percentage of the total zinc that remains in the residue. With a high-grade concentrate, a smaller percentage of zinc ferrite is usually formed during roasting because of the better separation of iron and zinc during the concentrating process, and because the iron and zinc are normally not in as intimate contact as in a low-zinc high-iron concentrate. Less sulphide sulphur remains in the calcine produced from a high-grade concentrate because of the higher roasting temperatures permissible in the absence of a relatively large amount of iron. The treatment of a concentrate containing a high percentage of zinc results in the formation of a smaller amount of insoluble zinc compounds during roasting; the smaller amount of insoluble zinc compounds formed results in a smaller amount of residue; and the smaller amount of residue produced decreases the loss of zinc sulphate as entrained solution, and allows more wash water to be used per ton of residue.

The amount of special residue treatment necessary to obtain a good over-all recovery of zinc must first be considered from the economic standpoint. While the several methods often used to recover zinc from the residue may be metallurgically sound, they may not be practical if conditions are such that it is cheaper to buy new concentrate than to treat the residue.

Regardless of the percentage of the total zinc concentrate that is contained in the residue, the residue may contain enough zinc economically to warrant special methods of treatment for its recovery. On the other hand, the loss of zinc, per ton of concentrate, in the residue may be excessive, yet the zinc content, per ton of residue, may be too low to pay for the cost of treatment. For example, assume that two concentrates are under consideration. The first contains 60 per cent zinc from which a recovery of 95 per cent can be obtained and from which 0.2 tons of residue is produced per ton of concentrate. This residue will contain 15 per cent zinc. The second concentrate contains 30 per cent zinc from which a recovery of 80 per cent can be obtained, and 0.65 tons of residue is produced per ton of concentrate. The residue from this concentrate will contain 9.25 per cent zinc. The residue from the first concentrate is an attractive one to treat, while the other is so low in zinc that conditions would need to be especially favorable for the value of the zinc extracted to pay for the cost of treatment.

Zinc ferrite is practically insoluble under the usual leaching conditions, and unless special recovery methods are employed, the loss of zinc in the residue is likely to be serious. A great many methods have been investigated and proposed for the extraction of zinc ferrite, but only a few have been found to be commercially feasible. The loss of zinc in the residue as zinc oxide, zinc sulphide, or zinc sulphate is large enough to receive some attention, but if an effective method of recovering zinc from zinc ferrite is used, the zinc in these other compounds is largely recovered in the same process.

Roasting the residue in an atmosphere of SO_2 gas at a temperature of 500 to 550°C. will convert most of the zinc ferrite to zinc sulphate, which is soluble in water. Some iron sulphate is formed during the roasting, and unless the temperature is raised above 600°C., iron will be extracted with the zinc by water leaching. By a careful regulation of temperature during the roast, the solubility of iron can be controlled to any desired degree. The reaction causing the decomposition of ferrite and the sulphating of zinc is probably due to the action of SO_3 gas. Ferric hydroxide decomposes at the temperature of the roast to form ferric oxide, which acts as a catalyst in converting a mixture of SO_2 and O_2 to SO_3 . The SO_3 so formed is then available for the sulphating reaction. This method was investigated during the early development of the zinc plant at Trail, B. C. The residue was treated in a multiple-hearth furnace, and pyrite was added to the lower hearths to furnish the SO_2 necessary for the decomposition of ferrite. This method was commercially successful for a time, but as the capacity of the plant increased, it was found to be rather slow for large-scale operations.

The "residue-fuming process" is another method used for the recovery of zinc from zinc-plant residue. This process depends on the decomposition of zinc ferrite and the formation of zinc sulphate when the residue is roasted with sulphuric acid at a high temperature. The reaction is probably carried out according to the equation: $\text{ZnO} \cdot \text{Fe}_2\text{O}_3 + 4\text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$. The sulphates of zinc and iron formed by this reaction are both soluble in a water leach. Some soluble ferric sulphate remaining in the finished product can be controlled by regulating the temperature of the roast. If the temperature is maintained above 600, but below 650°C., the ferric sulphate is rapidly decomposed into insoluble ferric oxide while the zinc sulphate remains practically unchanged.

A high recovery of zinc can be obtained by this method—75 to 80 per cent of the zinc in the residue—but there are two serious difficulties to be overcome. Evaporation of spent electrolyte to the concentration necessary to ensure sulphating is not a simple problem because zinc sulphate is crystallized out as the concentration increases. The solution can be depleted to about 5 g. per l. zinc before evaporation, but only at the expense of ampere efficiency. If a cheap source of commercial sulphuric acid is available, it may be more economical to deplete part of the spent electrolyte of its zinc content and to discard enough of this solution to offset the addition of fresh acid, than it is to evaporate spent electrolyte by ordinary means. The second difficulty to be overcome is the handling and roasting of the mixture of residue and acid. If all the acid necessary for complete sulphation is added to the residue at the start, the resulting mixture is too thin to be handled in the usual types of large-scale drying equipment.

Treatment of Copper-cadmium Residue.—The residue produced by purification of solution with zinc dust contains too much excess zinc dust to be discarded, and usually carries sufficient cadmium to pay for the necessary treatment to recover this metal. The copper content of this residue can also be recovered. Some basic zinc sulphate precipitated during the purification and clarification operations will be found in the residue. Unless the neutral-thickener overflow is filtered previous to purification, some recoverable zinc from slimes will also be present. The zinc from all these sources is just about equal to the amount of zinc dust used in the purification operation. Treatment of the purification residue is, then, necessary from the zinc-recovery standpoint, and is also desirable because most of the copper and cadmium can be recovered.

Purification residue is leached with dilute sulphuric acid (spent electrolyte) to dissolve as much zinc and cadmium as possible. The residue may be treated in either the oxidized or unoxidized condition. Oxidation, either by roasting or by long exposure to air, increases the solubility of zinc and cadmium to some extent but also increases the solubility of copper. If the residue is treated before complete oxidation takes place, the probable formation of arsine must be taken into account.

Oxidized purification residue is usually leached by adding the residue to the spent electrolyte until all the acid is neutralized. When leached in this manner, most of the zinc and cadmium is dissolved, and also a considerable portion of the copper goes into solution. The remaining sponge copper and insoluble material is settled out in thickeners, and is a desirable product for treatment by copper smelters. The thickener overflow, containing zinc, cadmium, and copper, is then treated with just enough zinc dust to precipitate all but a very slight amount of the copper present. The sponge copper from this operation is a desirable source of copper for use in the regular leaching operations; or it can be added to the first copper residue. The solution after being purified for copper is then treated for removal of its cadmium content. This can be done either by agitating with zinc dust, or by circulating the solution through tanks in which zinc slabs are suspended. In the first case, the action is much faster and is very satisfactory if a certain amount of zinc in the cadmium sponge can be tolerated. A cadmium sponge of greater purity is obtained by the use of zinc slabs. Most of the cadmium sponge in this case floats to the top of the solution and is removed by skimming. The sponge cadmium can be used for the production of cadmium metal. The solution, after the cadmium is removed, is sent to the main leaching system. If this solution contains an appreciable amount of undesirable impurity, such as cobalt, it is good practice to remove the impurity before returning the solution to the leaching system. Cobalt can be removed by the use of nitroso-beta-naphthol if the iron in solution is first precipitated. If the cadmium content of the solution is low, cobalt can be removed by sodium-ethyl-xanthate without any preliminary treatment.

If purification residue is treated with dilute sulphuric acid before much oxidation takes place, most of the zinc and cadmium goes into solution, but only a small amount of the copper is dissolved. The presence of a certain amount of metallic zinc and cadmium at all times causes the immediate reprecipitation of most of the copper, nickel, or cobalt dissolved. Settling or filtering a leach made in this manner results in a copper residue and a zinc-cadmium solution practically free from harmful impurities. The cadmium in the solution is precipitated, and the subsequent operations are carried out in the same manner as when oxidized residue is leached.

Purification residue may contain some arsenic, due to imperfect purification in the neutral leach. If the metallics always present in the freshly precipitated residue are not completely oxidized, then the treatment with acid will generate hydrogen. Hydrogen, when evolved in the presence of arsenic compounds, combines with arsenic to form arsenic hydride, commonly called arsine. Arsine is an extremely poisonous gas. A very little arsine, breathed into the human system, will cause serious illness or even death. It is, therefore, absolutely necessary to provide every possible safeguard in an operation of this kind. The purification residue treatment plant should be in a separate well-ventilated building. The leaching tanks should be hooded and connected to an exhaust fan of ample capacity to maintain a constant vacuum in the tanks and hoods. Samples of air should be drawn from different parts of the plant and tested for the presence of arsine. These samples should be drawn from near the surface of the settling tanks and, as arsine is heavier than air, from the low spots on the floor of the building. The tendency for arsine to collect in the low places is a dangerous characteristic. Unless every precaution is taken, it may collect unnoticed until some disturbance in the atmosphere of the building distributes it and poisons every employee in the department. A continuous test for the presence of arsine can very easily be made on the air samples drawn from various parts of the building. The air is first passed through lead acetate solution, to remove any H_2S that might be present, and then through silver nitrate solution. The presence of arsine in the sample causes the silver nitrate solution to turn black.

ELECTROLYSIS OF ZINC SULPHATE SOLUTION

Purity of Solution.—When the leaching and purifying operations have been properly carried out, the zinc sulphate solution delivered to the electrolyzing cells is almost entirely free from impurities that may be injurious to their operation. The electrolyzing cell is extremely sensitive to those elements which are electronegative to zinc. So marked is the action of certain impurities that they may have a detrimental effect on the cell when present in amounts too small to be detected by the regular methods. The effects of some impurities can be minimized by a change in operating conditions or by the use of certain addition agents, such as glue; but the only absolute guarantee of satisfactory results is purity of solution.

Next in importance to purity of solution is the purity of electrodes and tank-lining material. Pure chemical lead, or lead-alloy, anodes should be used. If the tanks are lined with sheet lead, only the purest lead obtainable should be used for this purpose. Aluminum of the highest purity should be used for the cathodes. A great deal of care should also be taken that no impurities accidentally find their way into the cell.

With the essential details taken care of, the electrolytic cell will allow a reasonably wide variation in operating conditions—such as temperature, acidity, current density, etc.—without much change in ampere efficiency. These conditions must, however, be considered in the economic success of the process as they are quite important in their effects upon the voltage required, and thereby on the power requirement.

Power Equipment.—Power is normally the largest single item in the operating cost of an electrolytic-zinc plant. Direct-current electrical power is necessary for electrolysis; and, in most cases, it must be converted from the alternating current supplied to the plant. The power requirement of the zinc cell is so great that the smallest possible conversion loss amounts to an appreciable sum in the larger installations. The size of the plant and the equipment available are the determining factors in deciding upon the conversion machine to be used. The gradual growth of the large zinc plants and the electrical equipment available at the time of the original capital outlay have resulted in the use of some conversion units which, if the ultimate size of the plant had been known, might not otherwise have been used. The conversion machines in general use are motor-generator sets, rotary converters, and mercury-arc rectifiers. Motor-generator sets are widely used in the smaller plants or where the growth of the plant has been gradual. They have a conversion efficiency of 85 to 88 per cent. Rotary converters, having suitable voltage control, are more efficient than motor-generator sets. The conversion efficiency of a large rotary converter is generally above 92 per cent and may be as high as 94 per cent. The higher voltage of the rotary converter permits more cells to be connected in series and requires fewer units. Larger and fewer units require less attendants and less floor space, making both first cost and operating cost less. Grounding the neutral point of each circuit lessens the possibility of personal injury with the higher voltage of the rotary converter. In over 25 years of operation at Great Falls, not a single injury has resulted from the exposure of over 200 workers per day to operating voltages of 500 to 550 volts. Mercury-arc rectifiers have a slightly higher conversion efficiency than rotary converters when operated at higher voltages than usually encountered in zinc plants. A factor of 94.5 per cent is obtained by the Magdeburg Zinc Works at Magdeburg, Germany, by operating mercury-arc rectifiers at 750 to 850 volts on the d-c side. Mercury-arc rectifiers have been in use for a long time; but only recent developments have given them operating efficiencies satisfactory to the zinc industry. A wider use of this type of conversion machine in the electrolytic-zinc industry can be expected in the future.

Tanks.—The tanks used as electrolyzing cells are usually constructed of wood, concrete, or pitch concrete. Many materials have been tried in the search for the "perfect tank," but very few have been found to possess enough of the essential qualifications to warrant their general use. The ideal tank should be relatively low in cost and give a long period of service. It should be a nonconductor and impervious to dilute sulphuric acid under electrolyzing conditions. It should be capable of carrying not only the load of solution, but also the weight of electrodes and tank bars.

Wood tanks were the first to be used for several reasons. Their ease of construction and apparent low cost were attractive, but the main reason was that during the early development of the electrolytic-zinc industry no better material was available. Wood tanks must be lined with lead or rubber to prevent leakage and to resist the action of dilute sulphuric acid. The wood used must be heavily creosoted to prevent rotting or disintegration due to the action of acid. The tanks must be well reinforced with tie rods and plates to withstand the load of solution and electrical equipment. Wood tanks are gradually disappearing and are being replaced by tanks constructed of materials having more of the essential qualifications of the ideal tank.

Concrete tanks must be lined with some material resistant to the corrosive action of dilute sulphuric acid. Lead, sulphur sand, or rubber are often used. Concrete tanks have a longer life and greater strength than wood tanks, but the cost is greater. They must be cast in wood or steel forms and aged 15 to 20 days before being put into service. Concrete is very susceptible to disintegration when in contact with acid; any leak developing in the lead lining is detrimental to the life of the tanks. This

effect can be partially prevented if the tanks are painted or varnished before lining, and if weep holes are provided in the bottom of the tanks. Nevertheless, this is a serious defect of concrete and overshadows many of the advantages of its use as a tank material.

Pitch-concrete tanks are, theoretically, the nearest approach to the perfect tank so far developed. They are a mixture of pitch, asphalt, silica rock, and silica sand. Pitch concrete has been used in Europe for several years for the production of acid-proof sewer pipe, tile, and the like; but its application to large castings was developed by the Consolidated Mining and Smelting Co., at Trail, B. C. Tanks made of pitch concrete are cast in one piece in steel forms. Special equipment is necessary for heating and mixing the material. Reinforcing wire and rods are used in the same manner as in reinforced concrete. When correctly made, pitch concrete equals concrete under compression, exceeds concrete in tensile strength, and does not require lead lining. The tanks are, however, quite fragile, and extreme care is necessary to



FIG. 7.—Great Falls tank house.

prevent cracks either from mechanical shock or from strains set up during the cooling period. Cracks when formed are quite difficult to repair. Several plants are now testing these tanks, but a long period of trial will be necessary before deciding whether this is the tank to be used.

The size of tank required depends on the number and size of the electrodes and the spacing between electrodes—4-in. spacing from center to center of anodes is about the maximum. Some space must be provided below the lower edge of the electrodes for settlement of the manganese dioxide sludge deposited at the anode. The space between the electrodes and the tank sides must be large enough to avoid striking the tank lining when the electrodes are removed. Overflow spouts of lead, rubber, etc., fastened either to the tank or to the tank lining at the lower end of each tank, are used to remove the spent electrolyte. No provision is made for draining the tanks from the bottom; it has been found cheaper and more satisfactory to empty the tanks for cleaning with a pump.

Electrodes.—Rolled aluminum sheets, $\frac{3}{32}$ to $\frac{3}{16}$ in. thick and of the highest purity, are used for cathodes. Copper support bars are riveted to the aluminum sheet; or copper inserts are cast into an aluminum header, which is then welded to the

sheet. Aluminum bars riveted to the sheets have been substituted for copper bars, but as electrical contact between aluminum and aluminum is not particularly good, excessive heating resulted. Sheets thicker than $\frac{3}{16}$ in. have been tried, but the added weight is an objectionable feature in removing plates for stripping. Wood, rubber, or rubber-lined aluminum strips are usually placed on the vertical edges of the sheets to prevent zinc building up around the edges. This serves the double purpose of eliminating the sharp edges where "trees" might form during the electrolysis and of increasing the ease of stripping. At Risdon, no strips are used; grooves are cut in the sheets along each edge to weaken the zinc deposit at these points so that the zinc can be more easily removed.

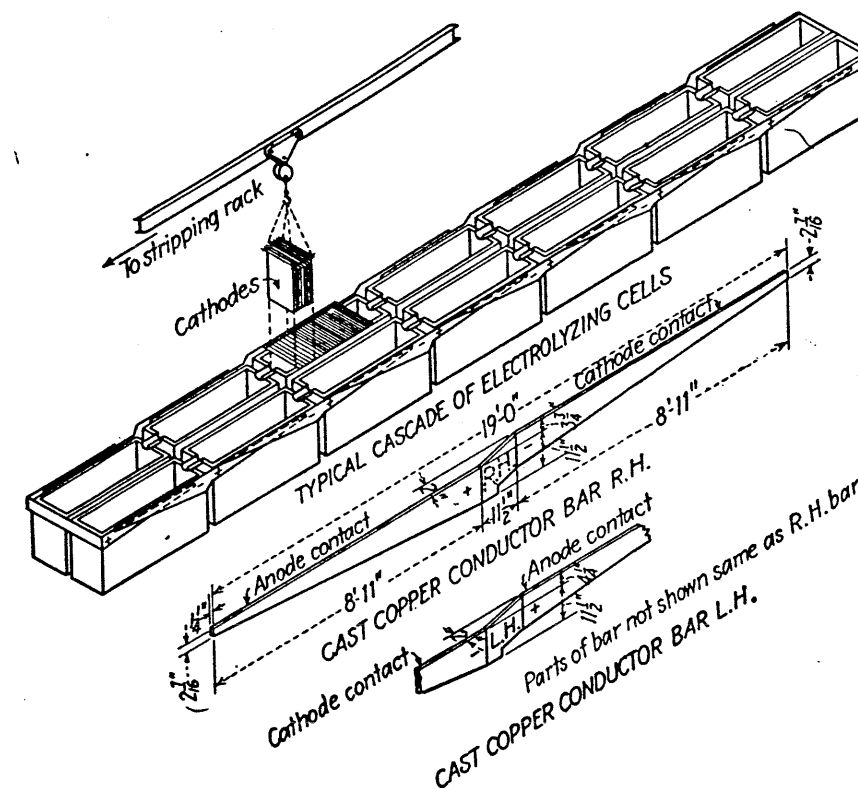


FIG. 8.—Bus-bar detail and arrangement.

The life of an aluminum cathode varies from 1 to 5 years, depending on the thickness of the sheet and the precautions taken to prevent corrosion. Most of the corrosion takes place just below the support bars. At the solution line, corrosion is considerably less, and below the solution line it is practically negligible. The life of the cathode can be greatly lengthened by using a sheet with a thicker cross section at the point of corrosion, or by riveting protecting plates of aluminum to the portion of the sheet above the solution line. The increased cost of fabrication and the high value of aluminum scrap have prevented the general adoption of the thickened cathode. The use of a paint or varnish that would stand up under chemical corrosion and mechanical wear would greatly prolong the life of the aluminum cathodes. Such a

paint or varnish has long been sought, but to date none of the many tested have proved commercially successful.

The anodes used in the zinc cell are of sheet lead $\frac{1}{8}$ to $\frac{3}{8}$ in. in thickness. Solid sheets are generally used, but perforated sheets are claimed to have some advantages. Where extremely close spacing of electrodes is practiced, some form of guide must be used to maintain this close spacing; and, because the circulation of solution is reduced by the guides, perforated anodes are almost a necessity. The anode sheets are usually cast, but rolled sheets may also be used. The anodes are generally cast around a copper header bar, leaving one end of the copper bar exposed to make contact with the tank bus bar.

Chemically pure lead, or an alloy of lead with silver, is used for the anode material.¹ Other alloying elements, such as cadmium, calcium, and arsenic, have been tested, but no element has been found to be as satisfactory as silver in preventing corrosion of the anode. Copper tends to build up in the lead when old anodes are melted and recast; it seems to have little effect on the anode in amounts up to 0.2 per cent.

The anode is the main source of lead in the cathode zinc, but the amount of lead plated out with the zinc is normally but a small part of the lead corroded from the anode. Most of the corroded lead remains as lead-manganese scale on the anode or settles to the bottom of the cell as a sludge. Both scale and sludge must be removed at regular intervals if the ampere efficiency of the cell is to be maintained, and if the lead in the cathode zinc is to be kept at a low level.

The length of time that an anode is used depends not only on the amount of corrosion of the lead, but also on the influence of the anode on the character and efficiency of zinc deposition. After a certain period of time, depending on local conditions, there is a gradual decrease in current efficiency and an increase in the amount of lead in the cathode zinc over that obtained with new anodes. When the optimum life of an anode has been passed, the anode is removed from the cell, melted, and recast. Some lead is lost during the melting as lead dross and must be replaced with new lead.

The size of the electrodes and the number used per cell depend on the capacity of the plant, the current density used, and other local conditions. Larger electrodes are required if the bus bars are carried on the edges of the tanks than if the bus bars are supported independently. This is due to the greater distance between the solution level and the electrode support bars. Spacing between electrodes in the cells varies from $\frac{5}{8}$ in., as at Kellogg, to a maximum of about 2 in. The electrodes must hang absolutely true to avoid short circuits and to ensure even distribution of current. Some sort of guide must be used, and the period of deposition must be shortened, when close spacing of electrodes is practiced.

The edges of the cathodes present sharp surfaces that tend to become points of higher current density than the rest of the surface. This effect is conducive to the formation of "trees." Anode sheets are usually made smaller than cathode sheets to reduce this effect. The use of strips on the vertical edges of the anodes helps to reduce the formation of "trees" and prevents undue warping of the anodes.

Bus Bars and Tank Bars.—Copper, either rolled or cast, is universally used for bus bars. Cast bars are usually cheaper than rolled, especially if odd shapes are required. The usual method of determining the size of bar required is to allow 1 sq. in. of cross-sectional area for each 1000 amp. With large bars, however, this does not allow enough radiating surface to avoid overheating. If 8000 to 12,000 amp. is to

¹ The lead-silver anode was originally worked out by U. C. Tainton, apparently largely from theory, and was a great factor in enabling him to produce four-9 and even five-9 zinc. The Tainton anode has about 40 per cent of its surface replaced by holes. For a description of the work on this anode, see Lead Alloys for Anodes in Electrolytic Production of Zinc of High Purity, by U. C. Tainton, A. G. Taylor, and H. P. Ehrlinger, *Trans. A.I.M.E.*, February meeting, 1929.—EDITOR.

be carried by the bar, the cross-sectional area allowed for each 1000 amp. should be at least 1.25 sq. in. Thus, cast-copper bus bars having a cross-sectional area of 10 sq. in. are recommended for a circuit carrying 8000 amp. The several lengths of bus bars are joined with machined lap joints bolted together. These joints must be inspected from time to time and the bolts tightened to ensure perfect contact; this is especially important during periods in which there have been large fluctuations in loads causing expansion or contraction.

Tank bars are used to connect the cell electrodes in parallel with each other and in series with the next cell in line. The greatest load, therefore, is at the center of

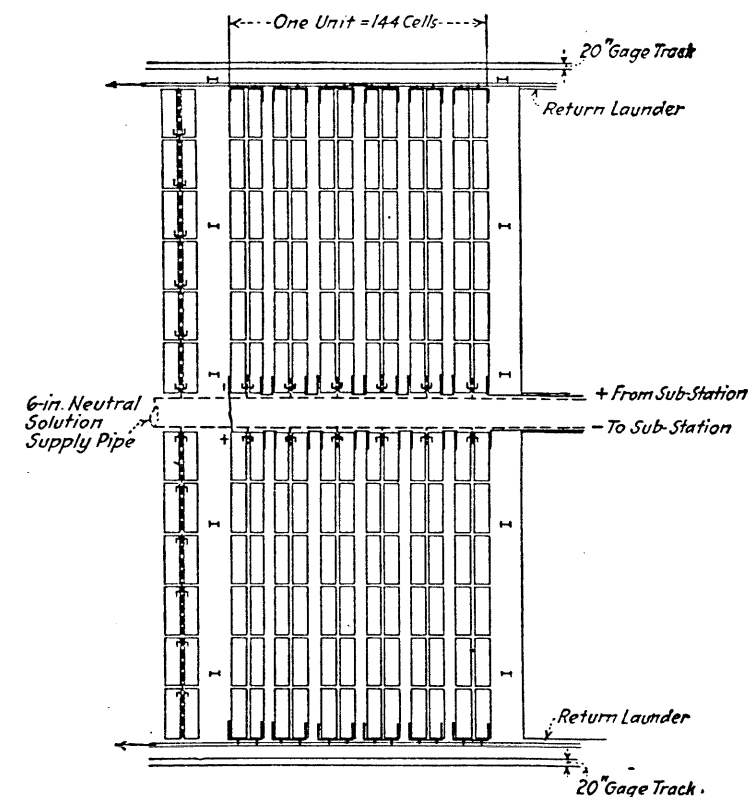


FIG. 9.—Tank layout, Great Falls.

the bar, and the smallest load is at either end. From the standpoint of first cost and working conditions, a bar larger in the center and tapering toward the end is the best. Then, at the point of connection to the main bus-bar line, the anode tank bar has the same area as the bar line, but, as the current is distributed to the individual anodes, the area decreases to a theoretical zero cross section at the end of the tank. The cathode bar starts at zero cross section and gradually increases in area as the load increases until it reaches the full area of the bar line and, passing to the next tank, becomes the anode bar and again gradually decreases to zero area. By using tapered bars and placing the bars on only one side of the tank, all bars in each group of tanks in solution series can be double bars. This system enables both the anode and the

cathode tank bars to be placed on the working side of the tank where they may be kept polished without leaning over the tank. The insulated ends of both the anode and cathode supports are in this case on the opposite side of the tank from the contact ends. The total amount of copper required on the tank with this system is only a little more than two-thirds of that required when using a common center bar, and about one-half that required if single bars are placed on each side of the tank.

Tank bars may be supported on the top edge of the tank, on the side of the tank, or by separate supports. When carried on the top edge of the tank, they are usually placed with the flat side resting on the supporting surface. When carried on the side of the tank, the normal practice is to place the bars on edge. In either case, the

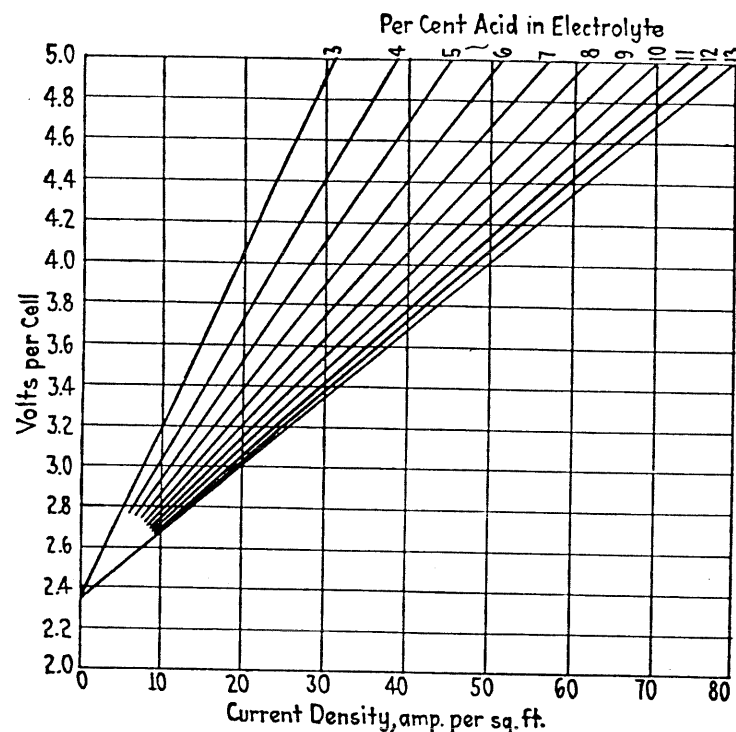


FIG. 10.—Cell resistances, 2-in. electrode spacing at 35°C.

outer bar is slightly higher than the inner so that contact can be made with the cathode or anode support bars without interference with each other. Separate support bars can be arranged in any manner to suit local ideas or conditions. The advantages of carrying the tank bars on the sides of the tanks are: a greater percentage of the electrode surfaces is rendered effective through reducing the space between the electrode supports and the solution level; contacts and tank-bar insulation are placed entirely outside the tank, simplifying the problem of keeping contacts clean and insulation dry; a smaller amount of acid mist or vapor comes in contact with the tank bar, reducing corrosion; a greater circulation of air around the bars is obtained, aiding cooling; and the copper sulphate formed by corrosion of the tank bars can be washed off without falling into the electrolyzing cell. The main disadvantage of the system is the necessity of supplying greater aisle space.

Insulation.—Tanks are insulated from their foundations by glass blocks or porcelain insulators between the tank supports and foundations. Wetting of these insulators by solution leaks can be prevented by covering them with sheet-lead caps. The electrode-support bars and tank bars are insulated from the tanks by wood strips and blocks impregnated with tar, oil, or other waterproofing material. Bus-bar lines are supported on glass or porcelain insulators or are suspended by some type of strain insulators from the tank-floor supports. Solution and water lines are insulated by the insertion of rubber-hose connections in the lines, and by supporting the lines on wood or tile blocks. All insulation must be of nonabsorbent materials to avoid wetting by condensation of water vapor from evaporation in the cells, and from the mist carried by gas from the cells.

Arrangement of Cells.—As many cells are placed in series, electrically, as the power equipment will permit. The maximum voltage limit of the direct-current

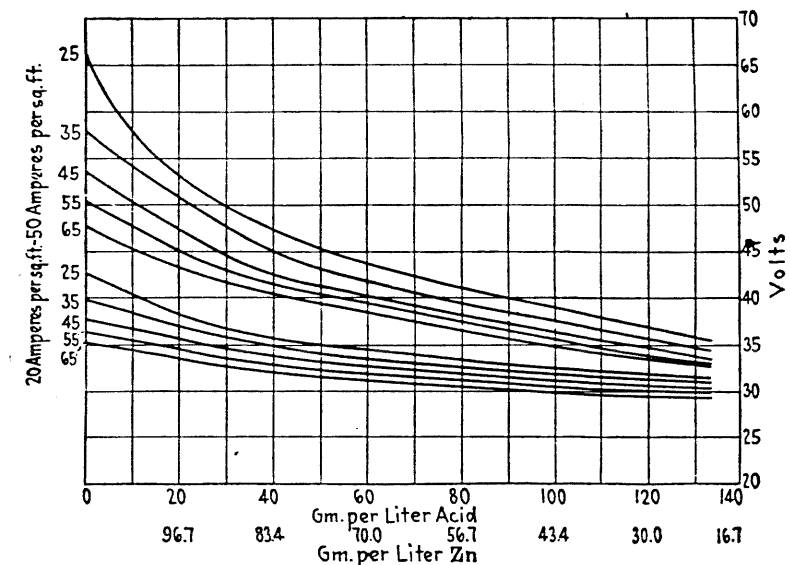


FIG. 11.—Electrolyte resistance, 4-in. anode spacing.

equipment divided by 3.75 is a safe figure to use in determining the number of cells to be connected to one power unit. The absolute maximum load should not be attempted as some leeway is desirable from an operating standpoint. Some of the earlier plants were designed for a maximum of 4 volts per cell, but this figure has been found to be too conservative.

As many cells may be placed in series or cascade, as regards solution flow, as is desired. Six to nine cells in solution series is the usual number. Working conditions and economy are the determining factors. The grouping at Great Falls and Risdon is in cascades of six cells. Twelve cells are placed side by side, as closely as safe insulation will permit, in a double row or cascade. This arrangement saves space as the working aisles are between each double row. Tank bars are placed on the sides of the tanks next to the aisles, leaving the inside tank edges for the insulated ends of electrode support bars. This arrangement is shown in Fig. 8. At Trail, the tanks are placed in a series of nine to a cascade. The two tanks side by side in each double cascade are constructed as a single unit with a common center wall.

By placing more cells in a cascade, less floor space and less copper are required; but the cathodes must be transported further for stripping, and more operating labor is necessary. It is customary, when tanks are to be cleaned, to cut a double cascade out of the electrical circuit at one time. Therefore, with the same number of cells per unit, the greater the number of tanks per cascade and the greater the proportion

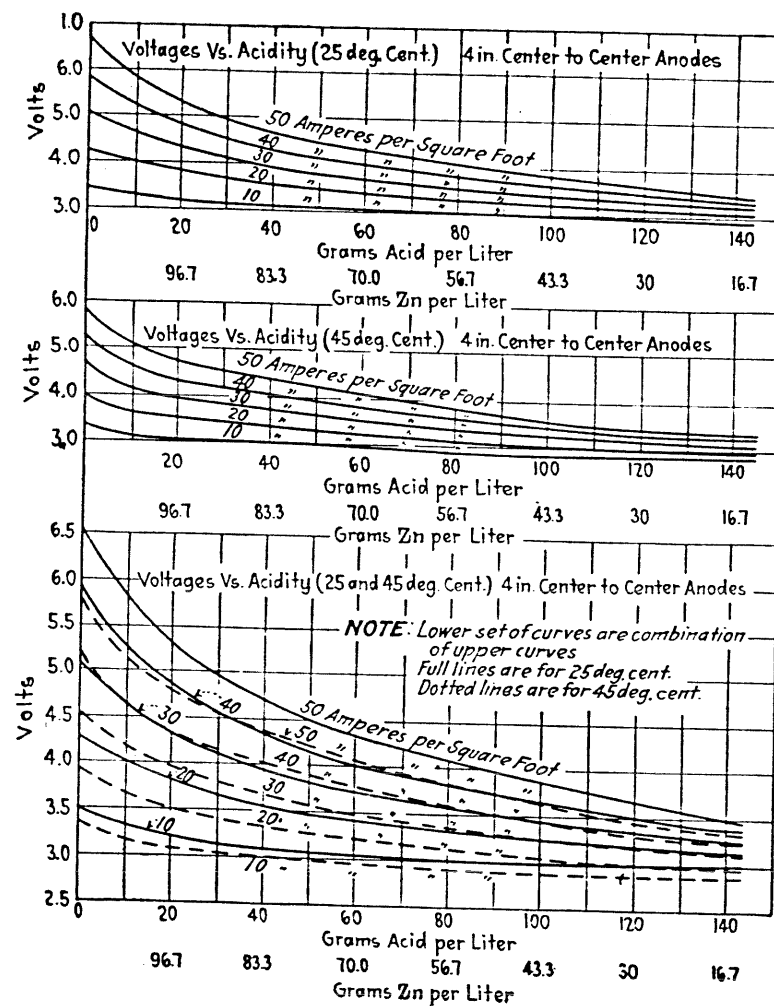


FIG. 12.—Electrolyte resistance.

of a unit cut out for cleaning. Any accidents, such as the breaking of a solution feed line over a tank or a leak in the roof of the building, which might wash impurities into a cell and contaminate the following cells in a cascade, are less serious if only a few cells are in series.

Solution System.—Solution to be fed to the electrolyzing cells is usually pumped into storage tanks placed at sufficient elevation to give a gravity flow from the storage

to the cells. Iron pipes may be used to conduct this solution to the cells as it is neutral in reaction and free from copper. Lead lines with flanged joints are preferable to iron, however, as some basic zinc sulphate and calcium sulphate are precipitated from the solution as cooling progresses, and build up in iron pipe more quickly than in lead. Also, there is always more or less danger of external corrosion of iron lines through occasional leaks of acid solution and by the condensation of acid mist from the cells. The feed lines are usually carried under the floor along the upper cells of the cascades, and a riser tapped in for each double cascade. A pipe line extending the full length of the cascade is connected to the riser, and each cell of the double cascade can be fed through branches equipped with valves to regulate the flow to each. Wood launders over the cells are used as header lines to carry the solution to the cells at the Magdeburg plant. The individual cells in this system are fed by means of rubber siphon hoses from the launder to the cells. The problem of regulating the flow in the launder to prevent spills and the extra space above the cells taken up by the launders prevent this system from being easily adaptable to the usual arrangement of electrolyzing cells.

At Great Falls, solution is fed into the head cell of each cascade at a rate that will maintain the acid strength in that cell at slightly less than the discharge from the last cell of the cascade. The first cell discharges into the head end of the second cell, the second into the third, and so on down the cascade. The last cell discharges into a launder that carries the spent electrolyte to storage tanks for the leaching plant. Neutral solution is fed into each cell but the last in sufficient quantity to maintain practically constant acidity throughout the cells, except the last, in a cascade. The last cell brings the acidity up to the desired strength or, from another viewpoint, depletes the zinc content to the desired point, thereby acting as a control cell. The acid content of each cell is determined at regular intervals and the feed to each cell so regulated as to give the desired acidity. By maintaining practically constant acidity in each cell, the voltage required is kept at a minimum. It is unnecessary to mix any acid with the neutral feed solution in order to keep the acidity of the upper cells up to the average. Each cell generates its own acid requirements and receives its own portion of feed, except that the lowest cell in each cascade usually receives only the discharge from the cells above it.

The rate of flow increases from the first to the last cell, the volume being cumulative; but no improvement in efficiency of the cells having the higher rate of flow has been noticed. No baffling arrangement is necessary to maintain an even distribution of solution in the cell as the gas evolution at the anode is sufficient to supply the necessary circulation. As the current density increases, the rate of zinc deposition increases, with an increased evolution of oxygen at the anode, and the gas evolved increases the rate of circulation proportionately to the requirement of fresh solution at the electrodes.

Cooling.—The electrolytic-zinc cell operates best at a temperature of between 35 to 45°C. A large proportion of the power delivered to the electrolytic-zinc cell is dissipated as heat, and the amount of heat dissipated increases with an increase in current density. Some heat is carried out by the spent electrolyte and some is radiated, but at the current density usually employed in practice, it is necessary to supply some additional cooling. This is usually done by passing water through coils placed in the cells. A current density of 30 amp. per sq. ft. or over requires at least 50 ft. of 1-in. cooling coil for each cell. The amount of cooling water passed through the coils depends on the temperature of the water and the efficiency of heat transfer in addition to the other cell conditions of current density, acidity, electrode spacing, etc. In any case the amount of cooling water needed is quite large and will vary from 6 to 8 gal. per min. for each ton of zinc produced per 24 hr.

Cooling coils are commonly made of lead, as most other materials that have been tried are not satisfactory either in their ease of construction, resistance to corrosion, physical strength, or ability to transfer heat efficiently. Two to four coils are used in the ends of each cell. Lead pipe of approximately 1 in. in diameter is usually used. The cooling water is not usually passed through a single coil, but two or three coils are placed in series in order to obtain the greatest possible amount of cooling from the water. The cooling water supply is carried in mains, which may be of iron pipe, but the connections between the main and the lead coils are made with short lengths of rubber hose which act as insulators. The actual amount of fresh water necessary for cooling purposes can be reduced by using a closed system and by passing the heated water through spray chambers. In this case the only additional water necessary is that needed to replace the amount lost by evaporation.

Stripping Equipment.—All methods of stripping the zinc deposit from the cathode—from removing one plate at a time to removing all the plates in a cell at one time—have been tried. The removal of one plate at a time is too slow and expensive, and removing a full tank at a time means a large loss of production and danger in "shorting" the tank before removing the plates. In addition to this, when all the plates are removed at once, some power-driven lifting device is necessary. If many plates are removed simultaneously, the current density on the remaining plates is greatly increased. If only one-third of the total plates are removed from the cell, the remaining plates are able to carry the current for the length of time necessary to strip the zinc.

At Great Falls the cathode sheets are lifted with hand-operated chain blocks running on I beams placed over the center line of each cascade. Nine sheets are lifted at a time, using a special rack. This lifting rack has sawtooth sides, and the teeth in the sides are spaced to correspond with the cathode spacing. The rack in use is placed on the cathode bars, and, as the load is raised, the spaces between the teeth on the rack engage lugs riveted to the cathode support bars. At the lower end of each cascade is placed a stand having nine pieces of 3-in. channel iron, the centers of which are spaced the same as the cathode spacing. A lengthwise slot is cut in the center of each channel iron into which a cathode sheet can be slipped and held upright. One end of each channel iron is bolted loosely to a supporting stand in such a manner that it can be moved in a horizontal plane. The load of cathodes is brought to this stand and the cathodes slipped into the slots in the channel irons. The load is lowered until the cathode support bars rest on the channel irons and the lifting rack is disengaged from the lugs. The outside sheet of zinc is removed from the first cathode; then the channel supporting that cathode is swung to one side, and the inside sheet of zinc removed from the same cathode. The adjacent side of the second cathode is exposed when the first is swung over. This second cathode is stripped on one side and then swung over and stripped on the other side. After all nine cathodes have been stripped in this manner, they are swung back into their original position and lifted with the lifting rack. The cathodes are returned to the cell from which they came, being held correctly spaced in the lifting rack.

A heavy knife is used for stripping the zinc deposit from the cathode. The deposit is struck a sharp blow at one corner with the edge of the knife to loosen it slightly from the surface of the aluminum cathode. The point of the knife is slipped under the loosened corner and twisted to break loose the deposit. If the zinc deposit adheres tightly to the cathode, a wooden mallet is sometimes used to aid the knife in breaking it loose. The zinc sheets, as stripped, are placed on small narrow-gauge cars. These cars are used to transport the cathodes to the melting furnaces.

Operation of the Cells.—Starting with clean cells, new electrodes, and neutral solution, the resistance of the zinc cells is so great that little current flows for several hours after power is put on the circuit. The addition of some pure acid, such as spent

electrolyte, immediately increases the flow of current by reducing the resistance. If no acid is available, the flow of current is permitted to increase as rapidly as decreased resistance, through the formation of acid, will permit. Some resistance may be removed by "shorting" one or two groups of cells in the unit until some current is flowing. It is customary, when starting up a unit from which the acid solution has been drained, to add some spent electrolyte to it from other units already operating. This shortens materially the time necessary to get the unit into normal production.

Starting with neutral solution, the zinc deposited in the first 24 or 48 hr. will be rather spongy. This condition is due to the low acidity of the cells; and the zinc deposit should be stripped as soon as it is thick enough to break loose from the aluminum blank. As soon as the deposited zinc begins to show a bright surface, the period of deposition can be increased to the normal length of time. When the acid strength gets up to 2 or 3 per cent, a small flow of neutral solution is started in the upper cells of the cascade and is gradually extended to the lower cells as the acidity increases, so that the solution in none of the cells becomes too low in zinc content. Acid strength is usually not allowed to get above about two-thirds normal until the full period of deposition is started. Full current density is generally not permitted until the deposited zinc has been stripped once or twice.

The amount of zinc stripped per man-day varies with the period of deposition and with the location of the plant. At Great Falls, using a 24-hr. period of deposition, each man cares for and strips the zinc from 12 cells. This is approximately 4 tons of zinc. At Trail, each man strips between 5 and 6 tons of zinc per day; and at Risdon, using a 72-hr. deposition period, each man strips between 8 and 9 tons of zinc per day.

Control of acidity is very important in the operation of the cells. Frequent tests of the acidity are necessary. These tests can be made by titration with standard sodium carbonate solution, by use of a hydrometer, or with an electrical-measuring device.

The electrolyzing cells must be periodically cleaned for several reasons. Many ores contain soluble manganese, and some manganese is used to oxidize iron in the neutral leach and is dissolved in the solution. Part of the manganese in the electrolyte is precipitated at the anode as manganese dioxide. Some of the precipitated MnO_2 adheres to the anode as a flaky covering, and the remainder settles to the bottom of the cell as a sludge. When the manganese dioxide in the cell exceeds a certain amount, depending upon the operating conditions of the cell, it must be removed. The insulation on top of the cells gradually becomes impregnated with solution and must be periodically renewed. The tank bars become covered with copper and zinc sulphates and must be cleaned at regular intervals. A double cascade of cells is usually cleaned at one time. The double cascade is cut out of the electrical circuit, the electrodes are removed, the solution is pumped out, and the manganese sludge is removed. The insulation is renewed, the tank bars are cleaned and replaced, the electrodes are cleaned, straightened, and replaced, and the cells are refilled with acid and solution. The double cascade is then put back into the electrical circuit. If a spare cascade is available, the cleaning cycle can be carried out in a systematic manner without loss of zinc production during the shutdown period.

Care of Workmen.—Rubber shoes should be supplied to insulate the men working in the electrolyzing room. Besides affording the worker protection from becoming "grounded" between the main circuit and the floor, the shoes also save him from a considerable amount of annoyance from stray currents which, although usually harmless, are always likely to be present. The acid solutions encountered in the electrolyzing room are very hard on garments made of cotton or mixed wool and cotton. The workmen in the cell room are usually given a clothes allowance or furnished clothing made of pure unwashed wool. Great care must be given the hands

of men coming in contact with acid zinc sulphate solution, otherwise cracks and sores, especially around the fingernails, will result. Rubber, or rubberized canvas, gloves are often used by the workmen. The spray rising from the electrolyzing cells is largely oxygen, but each bubble of gas is surrounded by a film of acid solution which is very corrosive to the nasal passages. Several thicknesses of sterilized cotton gauze placed over the nose and mouth will effectively filter out this spray. Each man should be furnished with fresh gauze every working day. No occupational disease has resulted from this work, nor has any extra trouble been experienced in obtaining men for this work.

A frothing-agent is added to the cells at Kellogg to prevent the formation of spray. This agent is very effective when used in a solution of small volume and high zinc content, but it is not satisfactory in a low-acid system.

Voltage.—The theoretical decomposition voltage of zinc sulphate solution is approximately 2.35 volts, but the best operating conditions require 3.25 to 3.50 volts, depending on current density, temperature, acidity, spacing of electrodes, and the period of deposition. With constant acidity, temperature, etc., the voltage increases rapidly with increased current density, as shown by Fig. 12. Resistance of solution is decreased by increasing acidity; this effect is quite marked up to 10 per cent H_2SO_4 , but proceeds more slowly above 10 per cent H_2SO_4 . With 30 amp. per sq. ft. current density, and with an acidity of 5 per cent H_2SO_4 , the voltage required is about 4.0 volts per cell at a temperature of 35°C. An increase in the acidity to 12 per cent, with all other conditions the same as before, reduces the voltage to 3.4 volts. If the temperature and the acidity are both increased, the decrease in voltage is even greater. High temperatures are not desirable in the electrolyzing cells from the standpoint of the increased effect of impurities on ampere efficiency. A high temperature is, however, advantageous in reducing the power cost of electrolyzing a solution low enough in impurities so that a good ampere efficiency can be obtained. In other words, it pays to supply the cells with a solution of sufficient purity so that a reasonably high temperature and acidity can be maintained. At Great Falls, a temperature of over 50°C. has been maintained for several weeks at a time with a current density of 30 amp per sq. ft. During these periods an ampere efficiency of 90 per cent was obtained when a deposition interval of 24 hr. was used.

The spacing between anodes and cathodes affects the voltage required for electrolysis, but cannot be safely reduced much below 2 in. without the use of special equipment to hold the electrodes in place. Electrodes have a tendency to warp during continued use with serious results if close spacing is used. Also they may not hang absolutely true, because of unevenness in the surface of the contacts between the support and tank bars, unless special guides are used.

Ampere Efficiency.—The ampere efficiency of electrolysis is calculated by dividing the actual yield of metal by the amount that theoretically should have been obtained from the current used. This result multiplied by 100 gives the percentage ampere efficiency of the process. One ampere-hour should theoretically deposit 1.219 g. of zinc from a solution. In actual practice, however, it is very seldom that an ampere efficiency of over 95 per cent of the theoretical is ever obtained for any length of time. At a current density of 30 to 40 amp. per sq. ft., an ampere efficiency of 92 to 94 per cent is considered good work. The factors that influence ampere efficiency in the operation of the zinc cell are the purity of the solution, the temperature of the cell, the effectiveness of addition agents, the period of deposition, and the ratio of zinc to acid in the solution.

Some harmful impurities can be present in much larger amounts than others without seriously affecting ampere efficiency. A great deal of work has been done to determine the effect of single impurities and to set safe limits for the amounts that

can be present in the solution without loss in current efficiency. The effect of any impurity, and the amount that can be tolerated, is strongly influenced by the other conditions that may be present during electrolysis. For this reason, the results of different experimenters do not always agree, but some fairly accurate averages have been obtained for the common impurities. The combined effect of two or more impurities, each present in an amount less than the safe limit for that impurity, is a much more involved problem than that concerned with the effect of single impurities. The

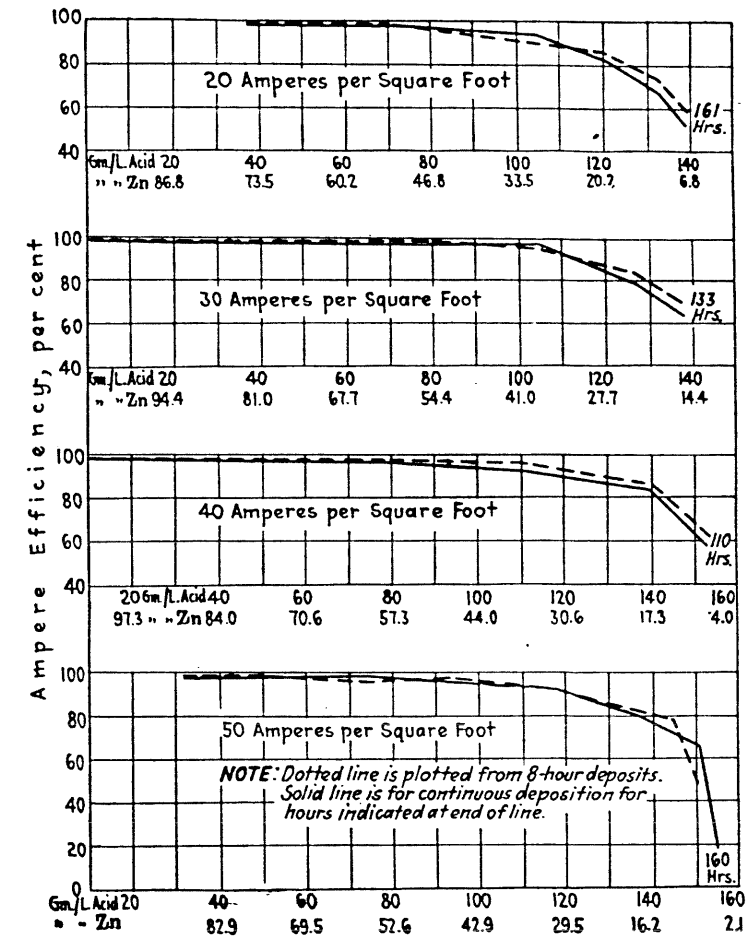


Fig. 13.—Effect of time of deposition and ratio of zinc to acid on ampere efficiency.

effects of some impurities, even in minute amounts, are greatly aggravated by the presence of certain other impurities. The enormous number of impurity combinations possible, when coupled with the many variations of operating conditions encountered in the process, prevents any easy solution of the problem. It may be that in the future some general rule relating to the problem can be evolved; but at the present time the information pertaining to the effect of impurity combinations deals only with certain specific conditions occurring in individual plants, and not generally applicable to the process.

The temperature at which the zinc cell operates is an important factor affecting ampere efficiency. The detrimental action of impurities is increased greatly, and the hydrogen overvoltage on zinc is lowered, by a rise in temperature. The optimum temperature for a zinc cell operating between 30 to 40 amp. per sq. ft. is usually to be found between 35 to 45°C. The operating costs required to cool the solution below 35°C. are usually more than the saving in ampere efficiency, while above 45°C. a good ampere efficiency can be obtained only when the solution to be electrolyzed is exceptionally free from impurities.

The period of deposition affects ampere efficiency; as the period of deposition increases, the effect of any impurity becomes more pronounced. With absolutely pure solution, high ampere efficiency can be obtained with 48-, 72-, 96-hr. or even longer periods of deposition. In plant operation it is frequently found advisable to decrease the period to 24 hr. or less. At Kellogg, using high current density, the period is 8 to 12 hr. Risdon, on the other hand, commonly operates with a deposition period of 72 hr., without any great loss in current efficiency. Most other plants use either a 24- or 48-hr. period. The length of time that zinc can be efficiently deposited is influenced by other cell conditions such as temperature, current density, acidity, and the effectiveness of addition agents. The most efficient period for each individual plant must be determined by balancing the extra labor cost for more frequent stripping against the power saved through improvements in ampere efficiency.

The ratio of zinc to acid in the solution necessary to maintain maximum ampere efficiency varies with all the other cell conditions. The usual practice is to deposit from solution about two-thirds of the zinc content of the neutral solution, and to return the other one-third to the leaching plant. If the amount deposited greatly exceeds this ratio, some loss in ampere efficiency will result. A cell in which the solution becomes greatly depleted in zinc has a tendency to evolve hydrogen. This condition can also be reached if the circulation of solution within the cell is not sufficient continually to supply all parts of the cell with an adequate amount of zinc ions. An excessive amount of circulation, however, is not desirable as it aids the rate of corrosion by increasing the amount of acid brought into contact with the deposited zinc. Here, as in the other operating conditions, the best rate of circulation must be determined experimentally.

Addition agents such as glue, goulac, and metal salts are often used to aid ampere efficiency and to improve the physical character of the zinc deposit. Glue is the most commonly used addition agent, but its use is becoming less as improved methods of purifying the solution are developed. It is not good practice to rely on the use of addition agents if it is possible properly to purify the solution to be electrolyzed. The addition of one impurity in order to inhibit the action of another is more in the nature of an evasion than a real solution to the problem. On the other hand, electrolytic-zinc plants must be operated at a profit, and any method to obtain the desired results should be employed until a better has been developed. Nearly all plants use some sort of addition agent at the present time. The presence of an unusual amount of cobalt in the electrolyte at Risdon, Tasmania, has made good ampere efficiency economically impossible without the use of addition agents. A combination of glue, beta-naphthol, and antimony is added to the electrolyte at Risdon, and ampere efficiencies of 92 to 94 per cent are obtained over a 72-hr. deposition period.

Another important factor that must be taken into consideration is the influence of workmen on ampere efficiency. Good workmen, conscientious in their care of the electrolyzing cells for which they are responsible, can consistently get higher efficiencies on their cells than can workmen who are somewhat careless. In some plants a bonus is paid to the workmen who, by careful attention to detail, are responsible for the production of more than a certain specified amount of metal.

Effect of Impurities.—The effects of single impurities on zinc electrolysis may be determined experimentally if certain necessary precautions are taken. In order to be certain of the results obtained, it is necessary to start with an absolutely pure solution of zinc sulphate; otherwise the result will be a combined effect of the added impurity along with those already present. A zinc sulphate solution prepared from the so-called c. p. zinc salts is not satisfactory for this work without further purification. The difficulty in applying any set of data on the effect of single impurities to actual plant operation is that a plant solution containing only one impurity is never obtained. Also, the experimental data are obtained with certain specified cell conditions which if varied cause a change in the effect of the impurity. These specified cell conditions are difficult to maintain with commercial operations on a large scale. The experimental data obtained have, however, been of great value as a basis from which to guide purification practice and as an aid to the recognition of the most injurious impurities. The experimental data have also enabled the operators to determine the presence of some impurities from the appearance of the zinc deposit without waiting for a complete analysis of solution.

The impurities encountered in the electrolysis of zinc may be classified, according to their general effects on the cell, as cathodic impurities, anodic impurities, and beneficial impurities.

Cathodic impurities have the greatest effects upon the efficiency of zinc deposition, and their elimination or control is one of the major problems in electrolysis. When a metallic salt is present in an acid solution and an electric current is passed through the solution, either the metal can be deposited or hydrogen can be evolved. When the decomposition voltage of the metallic salt present is above that of water, hydrogen is usually evolved. This is not true in the case of zinc, lead, or cadmium, however, owing to the high hydrogen overvoltage on these metals. In the case of zinc, the decomposition voltage of zinc sulphate is 2.35, and that of sulphuric acid on a zinc surface is 2.4. Therefore, zinc will be deposited at the cathode in preference to hydrogen unless, owing to the presence of certain impurities, the hydrogen overvoltage on zinc is lowered below the decomposition voltage of sulphuric acid. If any impurity, which lowers the hydrogen overvoltage on zinc to the point where hydrogen can be evolved, comes into contact with a zinc surface during electrolysis, hydrogen will be evolved on the surface of the impurity and zinc will be dissolved. The cathodic impurities can be further classified according to their effects on electrolysis. The first group includes those metals whose sulphates decompose at a higher voltage than zinc sulphate. The common elements of this group are aluminum, sodium, potassium, magnesium, and manganese. They have no effect on electrolysis so far as reactions at the cathode are concerned. The second group includes those metals whose hydrogen overvoltage is high enough not to cause the re-solution of zinc, but whose decomposition voltage is less than that of zinc. The common elements of this group are lead and cadmium. These have no detrimental effect on the efficiency of zinc decomposition; in some cases they may even be beneficial. They do, however, deposit with the zinc and cause an impure product. The third group includes those metals whose hydrogen overvoltage is below that of zinc but whose decomposition voltage is above that of sulphuric acid. The common elements of this group are iron, nickel, and cobalt. These metals are injurious to electrolysis, but do not ordinarily contaminate the deposited zinc. They are soluble in acid and consume power by being alternately deposited on the zinc surface and redissolved in the acid electrolyte. They are particularly detrimental to electrolysis when present in combination with certain other impurities. The fourth group includes those metals of which the sulphate decomposition voltage is below that of sulphuric acid and the hydrogen overvoltage is low enough to cause re-solution of zinc. Copper, arsenic, germanium, and antimony

belong to this group. They are deposited with the zinc and form points of low hydrogen overvoltage where hydrogen is evolved at the expense of the zinc. This group is the most injurious of all impurities. The commonly met cathodic impurities can all be classified in these four groups when present as single impurities; but combinations of two or more impurities, especially if from different groups, cannot be so easily classified.

The anodic impurities include all the anions except those of sulphuric acid. The common ions of this group are manganate, permanganate, chloride, chlorate, perchlorate, and fluoride. Their effect on electrolysis is not so violent as that of the metallic impurities, but they very often have a distinct bearing on the amount of corrosion occurring in the zinc cell. Some of them increase corrosion, and some aid in preventing it. Those anions which increase corrosion of the lead anodes cause an increase in the amount of lead deposited with the zinc. Those ions which increase corrosion of the aluminum cathode cause the deposited zinc to cling tightly to the sheet. This is commonly known as "sticking," and can become so intense that the zinc deposit can be removed only by dissolving in acid.

The beneficial impurities include all those used as addition agents. While these impurities may not be beneficial when used in an absolutely pure zinc sulphate solution, they are often used to prevent the more detrimental effects of certain other impurities. Some addition agents are beneficial in causing a smoother, harder deposit of zinc. Glue is an example of an impurity of this type. Manganese in the electrolyte accumulates on the anode in the form of manganese dioxide and tends to protect the anode from corrosion.

J. T. Ellsworth, at Park City, Utah, obtained data on the effects of single impurities that are as accurate as any that have yet been published. The results of his work were published in Volume 42 of the *Transactions of the American Electrochemical Society*. Ellsworth prepared a solution of zinc sulphate by burning zinc of high purity to form zinc oxide and dissolving this in pure sulphuric acid. This solution was then purified by agitation with zinc dust to remove the last traces of copper and cadmium. Definite quantities of each impurity tested were added to separate portions of the solution, and each was electrolyzed under a standard set of conditions.

Antimony is one of the most injurious impurities encountered in electrolytic-zinc operations. Its effect is noticeable at high temperature and high acidity if present in only minute amounts. One part per million is apparent even at the normal cell conditions of low temperature and acidity. The zinc becomes spongy and dark in color; sprouts, small at the surface of the zinc and large at the end, form in large numbers; and ampere efficiency is much lower. The longer the period of deposition, the greater will be the effect of the impurity. The remedies applied are a more thorough purification in the neutral leach, a shortening of the period of deposition, and a lower cell temperature. At Risdon, however, a small amount of antimony has been found beneficial when there is an unusual amount of cobalt in the electrolyte.

Arsenic, when alone, is much less injurious than antimony. The presence of arsenic in solution, however, is a pretty sure indication that some antimony is also present. Arsenic and antimony are both removed by the same methods of purification, but arsenic is eliminated more easily than antimony. Therefore, antimony may be present in small amounts without any arsenic, but arsenic is rarely present without antimony unless an ore free of antimony is being treated. The first indications of the presence of arsenic in the zinc cell are pronounced corrugation of the surface of the zinc deposit and the absence of the usual luster on the deposit. This is soon followed by sprouting and by a serious loss in ampere efficiency. There is really no excuse for the presence of arsenic in the electrolyte if efficient methods of control are used in the neutral leach.

Cobalt will cause re-solution when present in amounts as low as 10 mg. per l. unless special treatment is used. At Risdon, an addition agent consisting of glue, beta-

naphthol, and antimony is added to the solution in order to prevent the loss of current efficiency in the presence of larger amounts of cobalt than are usually encountered. Small amounts of cobalt can ordinarily be minimized in their effects by the use of glue alone. Cobalt is the most serious impurity commonly encountered in the process. While its detrimental effects are not so violent as a like amount of antimony, its removal is much more difficult. The pernicious influence of cobalt is much more marked when accompanied by germanium than when present alone. Small amounts of cobalt are eliminated by the regular methods of purification, but when present in large amounts it must be removed by special purification methods. Although cobalt lowers current efficiency, its presence in the electrolyte has a beneficial influence in lowering the amount of lead in the deposited zinc.

Germanium when present in amounts as low as 1 part in 10 million may produce adverse effects on the zinc deposit. Although very injurious when present alone, it is especially detrimental when accompanied by certain other impurities. For example, germanium in amounts too low to be detected by ordinary analytical methods will show a decided effect on electrolysis when cobalt is also present in the solution. Germanium, when present in small amounts, is usually eliminated by the iron hydroxide purification in the neutral leach. Some germanium is also removed by the regular zinc-dust purification if sufficient copper and cadmium are present. When present in any appreciable amounts, however, adequate removal of germanium requires special methods of purification.

Nickel has somewhat the same effect as cobalt. When alone, a concentration of 0.0001 g. per l. has no particular effect on ampere efficiency. Any amount above 0.0005 g. per l., however, is very injurious. Nickel causes the re-solution of the zinc deposit, and may also be found in the deposited metal. Nickel is not commonly found in appreciable amounts in zinc-plant solutions. When present, it can be removed with zinc dust if the solution is heated to a high temperature during the purification.

Copper may be present up to about 10 mg. per l. without much harm to ampere efficiency, and with a low acidity, the amount of copper may go even higher without serious results. If the usual methods of removing cadmium from solution are carried out far enough to produce high-grade zinc, there should never be any great danger of copper entering the zinc cell from this source. If uncoated copper support bars and tank bars are used, the corrosion of copper by the acid mist and by drippings must be considered as a source of copper in the cell. A great deal of care should be taken not to wash or knock the copper sulphate formed in this manner into the cells. The amount of copper so introduced is normally too small to affect the zinc deposit materially; but occasional breaks in water or solution lines, or leaks in the cell-room roof, may wash enough copper into a group of cells to cause violent re-solution in the cells affected. The quickest remedy for a condition of this sort is to run fresh solution into these cells in order to lower the acidity and to remove the fouled solution as soon as possible. The cathodes should also be removed and the deposited zinc stripped immediately to prevent it from going back into solution.

Cadmium, when present in amounts not to exceed 0.5 g. per l., does not lower ampere efficiency or injure the physical condition of the zinc deposit. In fact cadmium in small amounts has been claimed to increase ampere efficiency. Cadmium must, however, be removed from the solution previous to electrolysis if grade A zinc is to be produced. The elimination of cadmium is usually accomplished by the regular methods of purification.

Lead, like cadmium, is plated out with zinc during electrolysis. Lead sulphate is practically insoluble in zinc sulphate solution, and only very minute amounts are ever found in the solution fed to the cells. The greatest source of lead in the zinc cell is from corrosion of the lead anodes or the lead tank lining of the cell. Any factor, then,

that will reduce the corrosion of lead in the cell will lower the amount of lead in the deposited zinc. A further discussion of lead in cathode zinc will be found later under the heading Purity of Zinc Metal.

Iron in amounts up to 0.02 to 0.04 g. per l. has no noticeable effects on ampere efficiency. Above that amount, iron begins to cause trouble. Ferrous iron is oxidized at the anode to ferric iron, which in turn is reduced to ferrous iron at the cathode. This reaction takes power and in this way affects the ampere efficiency. Large amounts of iron, especially when other impurities are present, may become detrimental to the character and grade of the zinc deposit. The presence of iron in the electrolyte is usually an indication that the iron was incompletely precipitated in the neutral leach and serves as a warning that the impurities usually removed with iron may also be present.

Manganese is usually classed as a harmless impurity. It has no great influence on ampere efficiency unless present in amounts above 3 g. per l. Large amounts of manganese cause the zinc to form a rough spongy deposit with many beads and sprouts. Manganese is deposited at the anode during electrolysis. The reaction is partly an electrical deposition and partly a chemical precipitation. Manganese sulphate is partially oxidized at the anode to permanganic acid, which in turn slowly reacts with more manganese sulphate to form hydrated MnO_2 . This reaction is practically irreversible, and the precipitated manganese dioxide remains in the cell. Part of the MnO_2 adheres to the anode, and part falls to the bottom of the cell as a sludge. The amount that adheres to the anode seems to be dependent on the temperature and acidity of the electrolyte. The presence of certain other impurities such as iron or cobalt also influences the deposition of MnO_2 on the anode. Current density also seems to have some effect in this direction. Low acidity, low temperature, and low current density cause heavy anode coatings. If the amount of precipitated MnO_2 is so great that particles are occluded with the zinc deposit, these particles, being saturated with electrolyte, become individual cells. This "local action" is detrimental because large holes are formed in the zinc deposit.

Chlorine in amounts up to about 100 mg. per l. does not materially affect ampere efficiency. It does, however, increase the corrosion of lead anodes. Chlorides are easily oxidized at the anode to perchloric acid. Trail reports that the amount of perchloric acid formed is dependent on the oxidation potential of the anode. New anodes, for this reason, produce more than old anodes. Excessive amounts of chlorine may also have an effect on the cathode and cause the zinc deposit to adhere tightly. If the concentrate treated carries silver, the chlorine content of the electrolyte will usually be insufficient to cause trouble.

Fluorine has only recently been recognized as the chief cause of the zinc deposit "sticking" to the cathode. Any impurity or condition that causes corrosion of the aluminum cathode also causes sticking. The usual method of counteracting sticking is by conditioning the cathode to prevent corrosion. Various waxes, gums, and liquids have been used to produce a protective coating. The method used at Trail is to form a coating of aluminum sulphate on the cathode by a short "soaking" period in spent electrolyte. Fluorine is normally eliminated by the roasting process. There is no known commercial method of effectively removing fluorine from zinc sulphate solutions.

Nitrates, when present in the electrolyte, have much the same effect on the anodes as chlorides. Corrosion of lead is increased and the amount of lead deposited with zinc is larger when nitrates are present.

Sodium, potassium, magnesium, aluminum, calcium, etc., when present in the normal amounts, usually have no particular effect on ampere efficiency or on the physical character of the zinc deposit. Some of these elements are cumulative, however, and

if they build up to large amounts may become detrimental. At the Norway plant, for example, the concentrate contains so much magnesium that solution must be discarded at intervals in order to keep the magnesium content within satisfactory limits.

Current Density.—Current density is the strength of the electrical current used per unit of cross sectional area of the electrolyte. In the electrolytic-zinc industry, it is commonly expressed as amperes per square foot at the cathode. A wide range of current density may be used if all other operating conditions are properly adjusted. After a careful investigation of all the factors entering into the problem, all the large-scale producers have decided that a current-density range of 30 to 40 amp. per sq. ft. of cathode surface is the most economical and satisfactory density for their particular applications. Going much above 30 amp. per sq. ft. requires special provision for the cooling of solution and higher acidity to keep down abnormal power consumption. This higher acidity, in turn, requires a higher zinc content in the cell feed and is reflected in complications in the leaching system. If a current density much below 30 amp. per sq. ft. is used, the first cost of plant is high and the zinc deposited is not so firm as when deposited with higher densities. Local conditions determine the most economical current density for any particular installation.

An increase in current density is always attended by an increase in the power input to the cells because of the higher voltage required. The amount of voltage increase necessary will not be so great if the resistance in the cell is reduced by the use of a higher acidity and a closer spacing between the electrodes. When acidities above 12 to 13 per cent are to be maintained, the zinc content of the electrolyte must be higher than the saturation point of zinc sulphate at ordinary temperatures. Higher temperatures than usual must then be maintained in both the leaching and electrolyzing sections of the plant. High temperatures are beneficial in the purification and filtration steps of the leaching plant, but are often harmful in the electrolyzing cells. Settlement in the thickeners is hindered by an increase in density of the solution. Washing the residue after filtration is made more difficult by an increase in the zinc content of the solution, and the probable loss of water-soluble zinc is greater. If the resistance of the solution is reduced by closer spacing of the electrodes, the number of short circuits in the cell is likely to be increased. This condition adds to the cost of inspection and stripping. The effects of increasing current density under varying cell conditions are shown by the charts in Figs. 10 to 13. If the current density is increased much beyond the usual low-density practice, it might as well be raised to 100 amp. per sq. ft. or higher. The usual cooling equipment of a low-density cell room is not capable of sufficiently cooling the solution when high density is used. Also, if a current density higher than normal is used, special heating arrangements must be made in the leaching plant in order to prevent zinc sulphate crystallizing out of the supersaturated solution necessary to maintain the high acidity required.

Period of Deposition.—The period of deposition varies from the 8-hr. interval at Kellogg to the 72-hr. interval at Risdon. Shortening the period of deposition nearly always results in some increase in ampere efficiency, if all other conditions remain the same. When some harmful impurity is present, or if the temperature of the electrolyte is higher than normal, the effect of a variation in the deposition period is more pronounced than if the electrolyte is cool and of high purity. As the period of deposition is lengthened, the deposit gradually becomes rougher on the surface and tends to spring away from the surface of the aluminum sheet. The deposition period to be used is determined by balancing the benefits of increased ampere efficiency against the increased amount of labor required for more frequent stripping.

Purity of Cathode Zinc.—The purity of the zinc produced can be controlled partly by varying the cell conditions and partly by the amount of purification carried out

in the leaching plant. Purity of solution is the main factor influencing the purity of the metal. The impurity metals that deposit with zinc must be eliminated or controlled. The three impurities causing the most concern are cadmium, lead, and copper. The cadmium content of the zinc deposit is altogether dependent on the efficiency of the purification process. The lead content of cathode zinc is dependent both on the purity of solution and on cell conditions. The amount of copper in cathode zinc is almost entirely dependent on the amount of copper introduced into the cells by operating conditions.

The presence of lead in the deposited zinc is due mainly to corrosion of the lead anode. Normal electrolyte, when electrolyzed with platinum anodes, produces a deposit containing approximately 0.0002 per cent lead from soluble lead salts in the solution. The same solution when electrolyzed in a cell using lead anodes gives a much higher lead in the deposited zinc. The lead content of the deposited zinc varies with the operating conditions in the cell and increases with the age of the anode. If the lead anode is enclosed in a diaphragm, the amount of lead in the cathode zinc is greatly lowered. Any impurity, either in the solution or alloyed with the lead, that decreases the corrosion of the lead anode also decreases the amount of lead in the deposited zinc.

An ordinary lead anode consists of crystals of pure lead in a matrix of impure lead. This impure matrix is usually more soluble under the conditions of electrolysis than pure lead. As long as the crystals of lead are embedded in the anode, with a relatively small part of their surface exposed to the intense oxidizing conditions present at the anode, little lead peroxide is formed. When these crystals are set free, however, by solution of the matrix, they present a large surface to oxidation. Lead peroxide may either go into solution as lead persulphate and be deposited electrically, or it may be carried over to the cathode in the colloidal state and be occluded with the zinc deposit. When the anode is new, it takes some time before the matrix surrounding the crystals of lead is dissolved. During this period only a relatively small surface is presented for oxidation and the cathode zinc contains but little lead. If the anodes are replaced frequently, the quality of the zinc produced is improved. Any metal which, when alloyed with lead, tends to increase the resistance of the matrix to corrosion will lengthen the period during which the use of new anodes will produce a low-lead content in the cathode zinc. All the binary alloys of lead with the common metals have been investigated. A great many alloys containing two or more metals in addition to lead have also been tried.

The precipitation of manganese as a scale on the anode is often regarded as an aid in lowering the lead in cathode zinc. The formation of some scale is probably beneficial as a protecton against the action of certain anodic impurities. An excessive amount of manganese scale, however, tends to break away from the anode. This condition may become detrimental by mechanically carrying particles of lead peroxide to the cathode. The precipitation of manganese dioxide in the electrolyzing cell causes the eventual accumulation of a large amount of sludge in the bottom of the cell. Periodically the cells must be drained and this sludge removed. A frequent periodic cleaning aids in the production of zinc with a low lead content.

Any means of preventing lead dioxide from coming into contact with the cathode helps to lower the lead in cathode zinc. The use of a diaphragm surrounding the anode would be very effective in this respect, but no satisfactory form of diaphragm cell has yet been developed. The greatest detriment to the use of a diaphragm is the greatly increased corrosion of the anode caused by insufficient circulation in the cell. As soon as the diaphragm becomes partly "blinded" to free passage of the electrolyte, disintegration of the anode is enormously increased. An abnormal voltage drop between the anode and cathode accompanies this condition. Another, although

less serious, factor against the use of diaphragms in the zinc cell is the lack of a cheap satisfactory material.

The addition of any impurity to the electrolyte which will lower the oxidation potential at the anode is beneficial in the prevention of corrosion of the anode and aids in the production of low-lead zinc.

Miscellaneous Tank-room Notes.—Rotating-disk cathodes have been tried in place of stationary cathodes, with the hope of producing a heavier and smoother deposit. Their use has never been found to be satisfactory. Only about one-third of the rotating-cathode area is immersed in the electrolyte at one time; the remainder of the sheet is subject to re-solution of the zinc deposit by the adhering electrolyte. With disks of the required size, undue warping takes place, which results in the edge of the cathode coming in contact with the anode. Stripping the deposited zinc from rotating cathodes is a slow and expensive operation.

Starting sheets of zinc have been tried in place of aluminum depositing blanks, but have never proved successful. Thin deposits of zinc tear easily and, when dried, become quite brittle. The production, storage, and handling of zinc sheets is a difficult problem. Contacts between starting sheets and supporting bars cannot be made in a satisfactory manner. In operation the sheets tend to redissolve at the solution line, especially if the solution becomes slightly impure, causing the sheets to fall into the cells. The use of aluminum depositing blanks leaves little to be desired; they operate with so little trouble that no great incentive is given to the search for improved methods. The use of starting sheets would save in the cost of aluminum and would have some advantages because of the heavier sheet to be melted, but the experience so far with starting sheets has not been particularly encouraging.

If it becomes necessary to discard solution because of an overproduction of sulphate in roasting, the solution to be discarded should be depleted to less than 10 g. of zinc per liter. A separate group of cells should be used and a higher rate of flow than usual maintained in order to prevent overheating. The ampere efficiency on these cells will be much lower than normal, but the voltage will also be below average, and the actual loss in power will not be of any great consequence. Careful control of roasting conditions and a close cooperation among the various divisions of the plant, however, make it unnecessary to discard solution except under the most unusual conditions.

Melting and Casting.—Electrolytic zinc as cathode sheets has a very limited market. For most purposes the cathode sheets must be melted and cast into slabs. Melting must be done under carefully controlled conditions to prevent an excessive formation of dross. Casting of the molten zinc into slabs is a simple operation and can be done quite cheaply. The total cost of melting, casting, handling dross, and loading slabs for shipment amounts to only about 8 per cent of the total zinc production operating expenses, when hand labor is used for casting and loading.

A reverberatory furnace is commonly used for the melting operation. The depth of bath in zinc-melting furnaces is greater than is customary in similar furnaces for most other metals. The bath depth of the zinc-melting furnace varies from 30 to 36 in., depending on the area exposed for heating the bath. With a depth of 30 in., the hearth should be about 15 ft. wide by 20 ft. long. While, for construction purposes, a reverberatory furnace is commonly used, a furnace designed to transfer its heat to the bath from underneath would be better suited to the purpose than one heated through the surface of the bath. As much melting as possible is done under the surface of the bath. In the reverberatory furnace, the temperature must be carried so high to drive the necessary amount of heat into the bath that some burning of the zinc to zinc oxide is unavoidable.

The furnace is built on a steel pan to prevent possible loss of zinc through the furnace bottom. This steel pan is placed on concrete piers to allow a circulation of air under the furnace. The brick hearth is then built inside the pan. Common brick may be used for the bottom and hearth, but firebrick is necessary above the metal line and for the furnace roof. One or more charging holes, large enough to permit the passage of several cathode sheets, are built into the furnace roof. These holes are closed, except when charging the furnace, by remote-controlled cast-iron doors, usually water-cooled. Ladle wells, from which the zinc is ladled while casting, are built into one end of the furnace. These ladle wells are open on the bottom, and the sides extend below the surface of the bath to prevent dross from getting into the casting ladles, and to exclude air from the furnace. Doors are provided along the sides of the furnace, just above the metal line, for rabbling and skimming dross.

Casting is usually done by hand, using ladles carried from a trolley running on an overhead I beam. Each ladle holds a little over 200 lb. of molten zinc, which is enough to cast four slabs. The molds are made of cast iron, and the slabs cast in them each weigh 50 to 60 lb. The molds are placed on racks in a straight line under the I beam. Casting on a revolving wheel to carry the molds is not satisfactory because of the rough surface formed on the slabs by vibrations set up by the wheel. In order to obtain a bright smooth surface on the finished metal, the slabs are skimmed by hand as soon as they are poured. The slight film formed on the surface is removed by this skimming, along with any air bubbles during pouring. After the slabs are cast and skimmed, they are cooled by a water spray on the backs of the molds. As soon as the metal has "set," the molds, which are pivoted near the center, are turned over and the slabs dumped. The slabs are then stacked by hand and trammed away by either hand-drawn or powered trucks. A crew of three men can pour, skim, and stack 30 to 35 tons of zinc each working shift. With the larger furnaces, two or more ladle wells, ladles, and mold racks are usually provided.

Dross is skimmed from the furnace at regular periods into some suitable conveyance and is delivered either to a screening plant or to a "dross drum." In either case the object is to remove as much of the metallic zinc as possible from the dross. If the dross is to be screened, it is cooled before treatment; but if it is to be handled by a dross drum, it is delivered to the drum as hot as possible. The dross drum is a horizontal steel cylinder capable of being rotated on its longitudinal axis. The circumference of the drum is in the form of a modified scroll. When revolved in one direction, the charge is thoroughly mixed; but when the direction of the rotation is reversed, the drum empties itself. A drain at one end of the drum allows molten zinc, separated from the dross by action of the drum, to be drained off.

The metallic zinc recovered from dross is either returned to the melting furnaces or used for the production of zinc dust. This "treated" dross contains some mechanically held metal and also an appreciable amount of chlorine from the flux used in the furnace. The metallics must be oxidized and the chlorine reduced to a low figure before the dross can be returned to the leaching system. A separate furnace may be provided in which, by continued heating, the metallics are oxidized and most of the chlorine driven off. In many cases the dross can be sold as a separate product. Dross can also be reduced to zinc dust by reduction with coke in an electric furnace.

Furnace Operation.—Any fuel may be used with which a reasonable control of furnace atmosphere and temperature may be had. In order of preference, the fuels are gas, oil, and coal. A neutral or slightly reducing atmosphere should be maintained in the furnace to avoid burning the zinc. The temperature of the furnace gases should be kept below 600°C., preferably around 550°C.

Cathode sheets are charged into the bath of molten zinc through a charging door in either the roof or side of the furnace. As many sheets are charged at one time as

can be accommodated by the handling equipment and the bath of molten zinc. Some system such as rollers or slides is used so that the stack of cathodes can be charged with the least possible admission of air. As the stack of sheets falls into the bath, the individual sheets spread, allowing the molten zinc to pass around each sheet. If the furnace is large enough, more than one charging door may be provided, in order to spread the charge as much as possible. Ideally, the total charge should pass into the bath and out of contact with the furnace gases. Melting should take place under the surface of the bath. If the furnace is large enough, most of the heat necessary for melting is absorbed from the molten bath, which in turn receives its heat through the layer of dross on the surface of the bath. This ideal method of melting is seldom attained because of the large bath of metal necessary if 100 to 150 tons of cathode sheets is to be melted during each 24 hr. of furnace operation. In this case it becomes necessary to sacrifice some zinc by burning in order to maintain the necessary melting rate. Charging and casting are carried out simultaneously, and the level of the bath is held as constant as possible.

Some air is admitted into the furnace with each charging of cathode sheets, partially destroying the reducing atmosphere, and allowing a small portion of the zinc to burn with the formation of zinc oxide. A thin film of zinc sulphate is usually present on the surface of each cathode. The greater the amount of "sprouting" on the sheets, and the greater the porosity of the sheets—as when produced from an impure solution—the more air and zinc sulphate will be carried into the bath per pound of zinc. The zinc oxide produced in the furnace and the zinc sulphate from the sheets form a "dross" that rises and floats on the surface of the bath. This material holds within it a high percentage of metallic zinc and forms an insulating blanket that prevents efficient heat transfer to the bath. A small amount of dross on the surface of the bath is desirable as it protects the surface of the bath from further oxidation. The formation of a large amount, however, seriously affects the recovery of cathodes to slabs. Accumulations of dross in the furnace are removed at regular intervals. If the furnace is cooled down to prevent the burning of zinc and the dross is rabbled thoroughly, a large part of the metallic zinc held in the dross will drain into the bath. A small amount of sal ammoniac used as a flux aids in this separation by dissolving the oxide film surrounding the particles of zinc and allowing them to coalesce. An excessive amount of sal ammoniac should be avoided from the economic standpoint. Normal consumption of sal ammoniac is about 1 lb. per ton of cathodes melted. Rabbling also causes the formation of some oxide; the side doors must be open during the operation, admitting air to the charge; and a greater surface of zinc is exposed. After being thoroughly worked in this manner, and all the metallic zinc possible drained into the bath, the remaining dross is raked out through the side doors of the furnace. The dross is then either screened or treated in a dross drum. In the dross drum more sal ammoniac is added, and the resulting metallic zinc is allowed to drain out of the "dry" dross. A fairly complete separation is thus obtained, producing a dross containing about 80 to 85 per cent zinc. From 3 to 5 per cent of the weight of the cathode sheets charged goes into dross, the amount depending on the physical condition of the surface of the sheets, the crystalline structure of the metal, furnace operation, and the thoroughness with which the dross is treated for the recovery of metallic zinc. Less than 4 per cent dross is considered good work for average sheets. If the furnace capacity is exceeded, and it becomes necessary to melt a large part of the charge above the molten bath, it is almost impossible to prevent the formation of an excessive amount of dross.

Dross is a desirable source of zinc for lithopone, high-grade zinc oxide, and zinc chloride, much of it being used for these purposes. It is also a desirable material for some retort zinc smelters, requiring no roasting and enriching the lower grade zinc

materials treated. Its chlorine content is the only objection to returning it to the leaching division. If there is enough soluble silver in the calcine being treated to remove some chlorine from solution, roasting the dross at 400 to 500°C. will reduce its chlorine content sufficiently to permit re-treatment in the leaching division. If dross is to be re-treated, roasting, leaching, purification of solution, electrolysis, and melting of the resulting zinc must be charged against the amount of zinc recovered. Zinc dross may also be used for the production of zinc dust when reduced by suitable treatment in an electric furnace. Disposal of dross must be determined with respect to plant location and cost of re-treatment.

The flue gases from the casting furnaces carry a considerable amount of zinc oxide, which can be efficiently recovered by passing the gases through a baghouse. Cotton bags can be used if enough cooling pipes are used to cool the gases below 130°C. before entering the bags. The material caught is a mixture of zinc oxide and unburned carbon; it also contains an appreciable amount of chlorine from the sal ammoniac flux used in the furnace. This material can be disposed of in several ways: it can be water-leached to remove the chlorine and added to the leaching system, it can be added to the regular feed to the roasting furnaces, or it can be sold as a separate product.

Zinc Dust.—Zinc dust, for use in the purification of solution in the leaching division, is made by the atomization of molten zinc with compressed air. Molten zinc is transferred from the melting furnaces to a graphite crucible provided with a suitable heating arrangement to keep the zinc molten. The molten zinc, at a fairly high temperature, runs in small streams through holes in the bottom of the crucible, where it is immediately caught by a blast of compressed air, atomized, and blown into a settling chamber. The particles of zinc are cooled so rapidly that practically no oxidation takes place. Fineness of dust is controlled by air pressure, size of the stream of zinc, and the design and location of the air nozzle with respect to the stream of zinc.

The holes in the bottom of the crucible or pot, through which the molten zinc is carried to the air blast, are subject to a great deal of wear from the zinc stream. An increase in the size of the hole increases the size of zinc particles produced. It is therefore necessary to maintain as nearly as possible the original size of opening. This is accomplished by boring holes in the bottom of the crucible into which are cemented graphite plugs. These plugs are drilled for passage of the stream of molten zinc and are replaceable when the holes become too large. This results in a large saving in cost through a much longer crucible life.

The shape of the air jet formed by the nozzle or nozzles used in the atomization of zinc dust is of great importance in determining the efficiency of the operation. Multiple nozzles are much more satisfactory than a single opening. The air nozzles should form a jet which, if visible, would have the appearance of a U- or crescent-shaped trough in which the stream of molten zinc is caught. The bottom of the jet should be heavier than the sides. The air jet should converge to a point just beyond where struck by the molten zinc. If the stream of molten zinc strikes too far behind this point, some of the zinc will be carried up and out before becoming completely atomized; if too close to this point, the zinc stream will not be entrapped.

High air pressures give finer dust, but 75 lb. pressure will give a product most of which is finer than 100 mesh. The air supply to the jets must be well trapped to remove any oil carried over from the compressor; otherwise an explosion may occur in the dust-collecting system. Finely divided zinc dust in suspension is highly explosive, and particular care should be taken to keep open flames away from the dust plant.

If a classification of the zinc-dust particles is desired, sufficient air is drawn through the chamber into which the dust is blown to carry out the finer particles.

This fine dust is then caught by suitable collecting equipment. If no classification is desired, the chamber is vented through bags or other filtering equipment located over the chamber and discharging into it.

Zinc dust is usually produced only for local consumption, but is sometimes sold as a separate product. Because of the high purity and relative coarseness of the

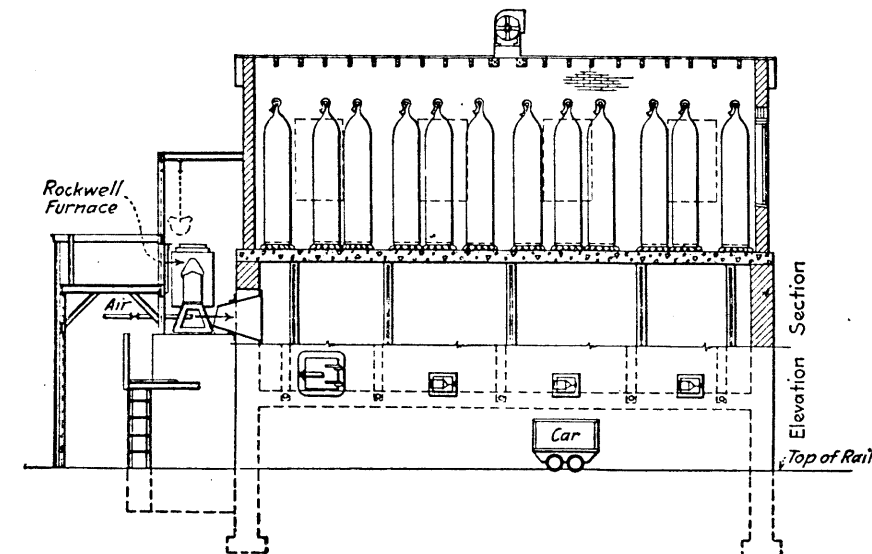


FIG. 14.—Zinc-dust plant.

usual zinc dust made by electrolytic-zinc plants, it is not entirely satisfactory for use in cyanide plants.

GENERAL PLANT DATA

Labor.—The total labor required for operation and maintenance, including everything from the unloading of the concentrate to the shipping of the finished zinc, will vary from 1.5 to 2.0 men per ton of zinc produced, depending on the capacity of the plant and the grade of concentrate treated. Low-grade concentrate requires more men in the roasting and leaching divisions, per ton of zinc produced, than high-grade concentrate. Increasing the capacity of a plant decreases the number of men required per ton of zinc. A high percentage of the labor required is what is usually termed unskilled labor. Working conditions are such that a good class of labor is attracted.

Power.—The actual power required for deposition of zinc at 30 amp. per sq. ft. will average about 1.5 kw.-hr. direct current per pound of zinc. Assuming 93 per cent conversion efficiency from alternating to direct current, approximately 1.6 kw.-hr. alternating current will be required per pound of zinc. This is 3200 kw.-hr. per ton of zinc. Auxiliary power for the roasters, leaching plant, casting, compressed air, etc., varies in its relation to the power for the electrolyzing cells with the size of the plant and the grade of concentrate being treated. For a plant producing 100 tons of zinc per day from a 50 per cent concentrate, the auxiliary power will amount to less than 10 per cent of the total power. This proportion of auxiliary power decreases as the size of the plant increases. Assuming 10 per cent for auxiliary power, the total power requirement for a 100-ton plant will be 3560 kw.-hr. per ton of

zinc, or a total of 15,000 kw. required. Decreasing the current density decreases the total power requirement slightly.

Auxiliary Equipment.—Leaching in 30-ton Pachuca tanks requires 125 to 150 cu. ft. of free air per minute per tank. This air is supplied at 20 to 30 lb. pressure. Some air is also required for agitation of pulp in filters, opening of thickener spigot lines, and various other purposes. It is desirable that air higher than 30 lb. per sq. in. should be furnished for these purposes. The manufacture of zinc dust requires an air pressure of at least 75 lb. per sq. in. The volume of air required for zinc-dust manufacture depends on the number of nozzles and the size of the stream being atomized. For all purposes, an average 100-ton plant should have a capacity of at least 1000 cu. ft. of high-pressure air per minute.

Some steam is used for heating solution in the leaching plant, in addition to the amount normally required for heating various buildings. The amount required for heating buildings will depend on climatic conditions and the type of building construction. Some heat is generated in the leaching tanks, the temperature averaging 50°C. or higher, and the large area exposed by the surface of the thickeners allows much of this heat to be radiated. This reduces the amount of steam heating necessary in the leaching plant. A similar condition exists in the electrolyzing division, but not much of this heat can be conserved because of the amount of ventilation required. No extra heat is required in the roasting and casting divisions beyond that needed to keep the air and water lines from freezing.

Water is required in increasingly large quantities, as the current density is increased, for cooling the cells. If the plant is so arranged as to permit proper distribution, the water for cooling the cells may be used again for all the other requirements of the plant. The only exception to this is the water used for cooling the transformers. The cell requirement—6 to 8 gal. per min. per ton of zinc daily output—is more than sufficient in volume for the other requirements. If reasonable care is taken of the cooling apparatus in the cells, the water will not be contaminated from this source.

A small foundry for making copper, bronze, and lead castings of spare parts, for replacement of equipment in contact with corrosive solutions, is almost a necessary adjunct to an electrolytic-zinc plant. It will prove to be a highly profitable investment. Carpenter, pipe, boiler, blacksmith, electric, and machine shops are needed to build and install new equipment and to care for the regular maintenance work.

First Cost of Plant.—The first cost of an electrolytic-zinc plant, including all auxiliary departments, water system, tramming systems, bins, etc., will vary from \$30,000 to \$40,000 per ton of daily zinc capacity. The cost depends on the size of the plant, type of construction, cost of labor and supplies, and the location of the plant. A large plant built under the most favorable conditions would probably cost about \$30,000 per ton of daily zinc output. A plant of only one-half the capacity of the larger, under the same conditions, would probably cost \$35,000 to \$40,000 per ton. Power-conversion equipment and motors make up the largest single item of cost. The second largest item is made up of electrolytic-cell equipment, such as aluminum cathodes, lead anodes, cooling coils, tank linings, copper bus bars, conductor bars, and other items made of copper or lead. Much of the leaching equipment is of copper, lead, or bronze. Roasting and leaching equipment is almost all of standard design and, for this reason, has a higher salvage value than if made specially for individual applications.

The first cost of an electrolytic-zinc plant depends less on the grade of material treated than that of a retort plant. The electrolyzing division and the melting and casting division are altogether dependent on the amount of zinc produced regardless of the source. Much leaching-plant equipment is dependent on the volume of solu-

tion to be handled and, therefore, on the zinc output. The roasting equipment necessary is largely dependent on the grade of concentrate. This is also true, to a large extent, of some of the leaching-plant equipment. The roasting equipment required for a given zinc production is roughly inversely proportional to the grade of zinc concentrate treated. The first cost of a plant of this kind, therefore, decreases as the grade of concentrate increases.

Recoveries.—If adequate means are provided to collect the dust from the roasting furnaces, the total losses in the roasting division will be almost negligible. The amount of dust carried out of the furnaces by the flue gases is usually high when roasting flotation concentrates in multiple-hearth furnaces, but is mostly a circulating load when proper equipment is used. The only other source of loss in the roasting department is through screening and cooling of the calcine and in crushing oversize calcine preparatory to returning it for further roasting.

The leaching-plant residue contains unroasted zinc sulphide from the calcine, zinc ferrite insoluble in the leaching process, some zinc oxide not dissolved in the leaching solution, and any zinc sulphate not removed when the residue is washed with water. The total loss of zinc as residue is the largest single loss of the electrolytic process and may account for as much as 20 per cent of the total zinc with a particularly unfavorable zinc ore. The loss of zinc as ferrite is usually the main part of the residue loss. In case of very pure ores, however, the loss of zinc as sulphide may exceed the loss as ferrite. Any unroasted zinc sulphide carries approximately twice as much zinc as sulphur. A 0.2 per cent sulphide sulphur in the calcine, therefore, will mean a loss of 0.4 per cent zinc, which is equivalent to 1 per cent of the total zinc in a 40 per cent concentrate. A concentrate containing much iron will produce a correspondingly high percentage of residue with a large loss of zinc as ferrite. As has been previously pointed out under the discussion of the formation of ferrite, the amount of ferrite formed cannot be definitely predicted from an analysis of the concentrate because of the fact that the intimacy of contact between the particles of zinc and iron influences the completeness of combination. It can be assumed for general purposes, however, that as the iron content of the concentrate increases, the amount of zinc ferrite loss in the residue also increases. The real measure of efficiency of the leaching process is shown by the amount of undissolved zinc oxide remaining in the residue; good operation requires that the amount of such zinc in the residue should be less than 5 per cent of the total zinc in the residue. When treating a concentrate containing approximately 55 per cent zinc, the total zinc in the residue should not be more than 6 per cent of the zinc in the concentrate; of this amount, 8 per cent—or about 0.5 per cent of the zinc in the concentrate—will be present in the residue as zinc oxide. The amount of zinc lost in the residue as zinc sulphate will be approximately twice that lost as zinc oxide. In other words, about 10 to 20 per cent of the total zinc in the residue, or about 1 per cent of the zinc in the original concentrate, will be lost in the residue as zinc sulphate. The normal zinc loss in residue from a high-grade concentrate containing 55 per cent zinc may be summed up as follows: 0.2 per cent of the sulphur unroasted will cause a loss of 0.7 per cent, undissolved zinc oxide will cause a loss of 0.5 per cent, zinc sulphate not washed from the residue will cause a loss of 1 per cent, and the insoluble ferrite will cause a loss of approximately 3.8 per cent. This is a total loss of 6 per cent. As the zinc content of the concentrate decreases, with a corresponding increase in the iron content, the percentage loss from sulphide and ferrite will increase, and the percentage loss as zinc oxide and zinc sulphate will decrease. With a concentrate containing 40 per cent zinc, the residue loss will amount to about 12 per cent of the total zinc.

Figure 15 gives a formula for determining leaching recovery (recovery from calcine to residue). It is based on the fact that the amount of zinc in a definite amount of

calcine that is insoluble in 1 per cent H_2SO_4 equals the amount of such insoluble zinc in the residue produced from this calcine. The recovery calculated from this graphic formula does not include any loss in purification residue.

The amount of purification residue produced and the amount of zinc in such residue depend mainly on the amount of copper and cadmium in the solution to be purified, and therefore on the amount of zinc dust used for purification of solution. The purification residue also contains some basic sulphate precipitated from the solution, and solids overflowing the neutral thickeners. The amount of zinc from these sources makes the zinc content of this residue approximately equal to the

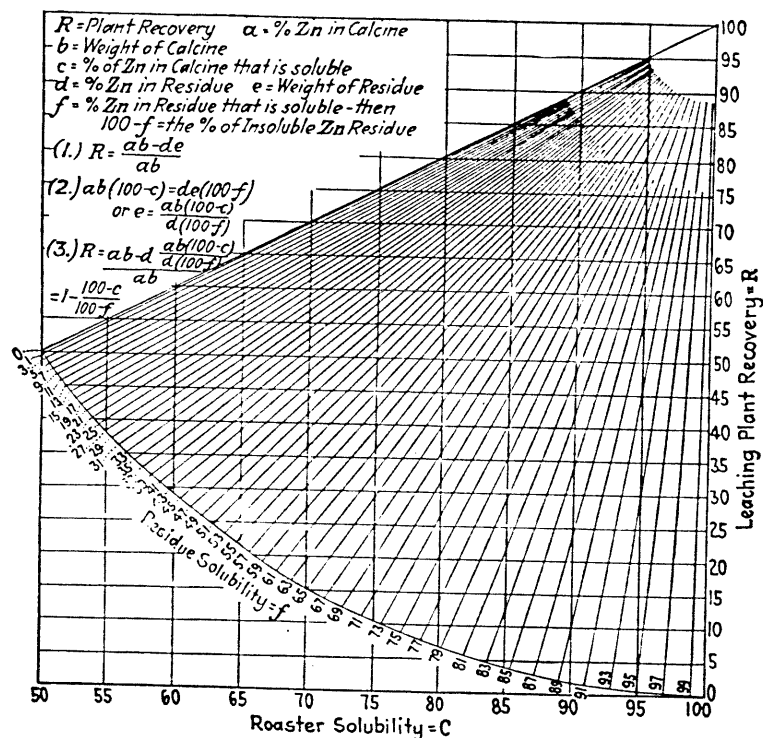


FIG. 15.—Graphic zinc-recovery formula (based on fact that insoluble zinc in calcine equals insoluble zinc in residue).

amount of zinc dust used for purification. Treatment of the purification residue for the recovery of the zinc and separation of the copper and cadmium will recover 90 to 95 per cent of the zinc content. With adequate treatment, the net loss of zinc from this source should not be more than 10 per cent of the zinc dust used.

There is no loss of zinc in the electrolyzing division, other than that from mist or spray from the surface of the cells, unless acid is discarded. With careful control of roasting and leaching operations, there is really no necessity for discarding acid. Even if it does become necessary for a plant to discard some acid, the loss of zinc from this source can be minimized by depleting the zinc in this solution to 1 per cent or less.

If the dust in furnace gases is properly collected, there should be practically no zinc loss in the melting and casting division. The only loss in this case is a result of handling and treating the collected dust and the zinc dross produced by the melting

operation. The total loss in this division should not be more than 0.10 per cent of the total zinc entering the plant.

There is always some loss of zinc through handling solution and calcine. The total loss from handling should not be much; the amount depends on the arrangement of the plant divisions and on the provisions for handling occasional spills of solution. The sum of all such losses in the leaching and electrolyzing divisions should not exceed 1.0 per cent of the total zinc loss.

Starting with a concentrate containing approximately 55 per cent zinc, 0.6 per cent copper, and 2 per cent iron, the expected losses should be about as follows: roasting, 0.75 per cent; leaching-plant residue, 6.0 per cent; purification residue, 0.25 per cent; melting and casting division, 0.10 per cent; general handling, 1.0 per cent; total, 8.1 per cent. This is an over-all recovery of 91.9 per cent from concentrate to finished zinc.

By-products.—The location of the plant with respect to markets for the sale of by-products limits the value and the production of these materials. Common by-products, which may be produced in connection with regular plant operation, are sulphuric acid, zinc dust, zinc oxide, lithopone, zinc salts, cadmium, and cadmium salts.

Sulphuric acid can be profitably produced from the roaster gas of an electrolytic-zinc plant if a satisfactory market exists for this product. When high-iron concentrates are to be treated, however, close temperature control is required and the upper hearths of the furnace must be kept cool by the admission of air to prevent the formation of an excessive amount of ferrite. A condition such as this renders the production of sulphuric acid unprofitable unless the value of the by-product is such that it is cheaper to provide some special method of residue treatment to recover the zinc combined as ferrite and to produce acid from the roaster gas.

Some sulphuric acid is produced by sulphate roasting and the subsequent electrolysis of the resulting zinc sulphate. More or less zinc sulphate is formed depending on the conditions of roasting. Also, if the iron sulphate formed during roasting is not decomposed in the lower part of the furnace, the SO_4 radical will unite with zinc to form zinc sulphate during the reactions in the neutral leach by which iron hydroxide is precipitated with excess zinc oxide. This is a source of sulphuric acid; but acid is expensive to produce in this manner, as the spent electrolyte must be evaporated in order to obtain a marketable product. If, however, a market is also available for lithopone or zinc sulphate, such acid can be profitably utilized.

Zinc dust is produced primarily for the purification of solution. The high purity and relative coarseness of the dust normally used for this purpose makes it undesirable for market purposes. There is no objection to the use of dust containing some lead and cadmium in the regular zinc-dust purification. Therefore, if a suitable market exists, it is very easy to lower the purity of the dust produced without affecting the efficiency of the dust used for local consumption. The dust can also be produced in any desired degree of fineness by slight changes in the atomizing process and by classifying the dust while it is being collected.

Zinc dross is very often sold as a by-product of the electrolytic-zinc process. Much of it has been used in the production of lithopone, high-grade zinc oxide, and for zinc chloride. Zinc dross is also a desirable material for some retort smelters as it is very high in zinc content and requires no preliminary treatment. Whether zinc dross is sold as a by-product or re-treated for the production of zinc depends on the location of the plant and the existing markets.

Zinc sulphate solution suitable for electrolysis is of a high degree of purity except for manganese. When manganese has been removed by the usual methods, the resulting solution is of exceptional purity and is highly desirable for the production

of lithopone. The acid combined with the zinc costs practically nothing to produce, and the zinc may be figured to be worth the market price at the plant less the cost of electrolysis, melting, and casting. If the plant considering the sale of zinc sulphate for this purpose regularly discards acid from the system, the production of lithopone, in an amount just sufficient to offset the necessary depletion in acid content, could be credited with the saving in power and zinc loss resulting from the discarding of acid. Zinc sulphate can be produced by the evaporation of regular plant solution.

Cadmium metal has become one of the main by-products of the electrolytic-zinc process. Practically all ores of zinc contain small quantities of cadmium. In the metallurgy of zinc it is necessary to remove the cadmium from the solution previous to electrolysis if high-grade zinc is to be produced. The cadmium is first eliminated from the regular zinc cycle in the purification residue. During the treatment of purification residue for the recovery of zinc and copper, the cadmium is usually precipitated from solution as an impure sponge metal. From this state it is but a simple process to produce cadmium metal suitable for market. A further advantage in producing cadmium as a by-product of the electrolytic-zinc process is that the main portion of the expense is borne by the zinc plant.

The impure cadmium sponge is stored in stock piles for several days to allow partial but not complete oxidation. This process of oxidation may be speeded up by piling the sponge on a large heated pipe. Unoxidized cadmium sponge is slow to dissolve in dilute sulphuric acid, but when oxidized it will dissolve very rapidly. The oxidized sponge contains zinc, lead, iron, cobalt, nickel, and sometimes thallium as impurities. All these, with the exception of zinc, must be removed previous to electrolysis of the cadmium solution. The sponge is dissolved in return electrolyte from the cadmium electrolyzing cells, in spent electrolyte from the zinc cells which have been depleted in zinc, in commercial sulphuric acid diluted with water, or, as is quite often the case, in some combination of these acids. The leach is neutralized with a large excess of the incompletely oxidized cadmium sponge and, owing to the presence of some metallic cadmium, most of the impurities are eliminated by replacement with cadmium. The leach is then filtered, and if necessary, further purification steps are carried out to eliminate any especially troublesome impurities still present. The solution after purification, for best results, should contain 180 to 220 g. per l. of cadmium. The solution may also contain zinc in an amount not to exceed 50 per cent of the cadmium content without detrimental effects to the electrolysis of cadmium.

Cadmium is difficult to electrolyze because of the formation of trees and sprouts. The formation of trees and sprouts can be minimized by keeping the cadmium content in the electrolyte relatively high. The cell and electrodes in the cadmium electrolysis cell are practically the same as in the regular zinc cell. The cells are fed with solution individually and are not in cascade. Glue is added to prevent the excessive formation of beads. The current density used in the cadmium cell ranges between 2 and 15 amp. per sq. ft.

The deposited cadmium metal is stripped from the cathodes each day and rolled into bundles for melting. The bundles are melted under a layer of caustic (NaOH) in large iron pots, and cast into slabs weighing approximately 75 lb. each. These slabs are remelted and cast into shapes for market. The usual shapes are balls, pencils, slabs, or special anodes.

Residue Treatment.—Leaching-plant residue as discharged from the filters contains a high percentage of moisture. The moisture content varies from 20 to 35 per cent according to the amount of gelatinous material precipitated in the neutral leach, during the purification of iron, silica, alumina, etc., in comparison with the amount of sandy material in the residue. The presence of relatively coarse material is of considerable benefit in the filtering and washing operations and aids in producing a

low moisture content by keeping the cake "open" to passage of the solution and wash water. High-grade zinc concentrate produces a residue high in moisture because the amount of gelatinous material produced from such a concentrate is high in proportion to the amount of sandy material in the residue. As a general rule, the amount of sandy material increases as the zinc content of the concentrate decreases. To be suitable for the usual methods of treatment, the residue must be dried further to reduce the moisture content.

A direct-fired rotary drier has a large capacity and is cheap to operate, and is superior in these respects to other types of drying equipment. It consists of a brick-lined steel tube mounted on rollers at a slight incline and revolved by a gear-and-pinion drive. The material to be dried is introduced through a chute at the upper end and, because of the revolution of the inclined tube, slowly passes through the drier to the lower end where it is discharged. The tube is fired at the discharge end, and the hot gases leave the drier at the feed end.

Part of the drying is done by contact between the residue and the hot gases and part by contact between the residue and brick lining. The lining is exposed to the hot gases for more than half of the revolution and absorbs heat that is later transferred to the residue. The revolving motion of the drier carries the residue part way up the side of the tube in the direction of rotation, and then the material falls or rolls back into the trough. A good contact between the residue and the hot gases is given because of this action. The rolling action of the drier gives a product that is formed into small lumps or balls. This product can be handled without excessive dusting loss and does not tend to hang up in bins or hoppers. The dried material contains 10 to 15 per cent moisture. The apparently high moisture content is due to incomplete drying in the centers of the lumps. Further reduction in the moisture content is not desirable with this type of drier, as an excessive dust loss from the driers and in handling would result; if a lower moisture content is necessary, some other type of drier should be used.

The methods of treating the final residue from the electrolytic-zinc process are many and varied. Lead-furnace or copper-furnace treatment of the residue, or a combination of the two, is the usual procedure if the zinc plant is situated in a locality where these methods are economically available. Some wet methods have been employed in the past for residue treatment but, as they are not entirely satisfactory, are not now in common use. The margin of profit in treating the final residue is so low that not many special methods have been developed; several methods have, however, been adapted from other metallurgical process. Among these several methods are the Waelz process, the ash-fusion process, and the electrothermic process.

Classes of Residue.—Residue may be divided into four general classes: (1) that containing insufficient values to pay for the cost of further treatment; (2) that containing lead as the only value of consequence in deciding the method of treatment; (3) that in which metals other than lead are present in considerable amounts, but in which lead is in excess of copper in value; and (4) that in which the value of recoverable copper exceeds the value of recoverable lead.

The residue from class 1 is a waste product and may be discarded by countercurrent washing and sluicing. This method of disposal will save some of the cost of filtering and repulping. The difference in cost between countercurrent washing and the usual filtering and washing operation offsets the loss of value in the residue. The economics of the two methods for the disposal of a class 1 residue must be considered in the light of local plant conditions before deciding which is the most desirable method for any individual situation. The point at which to draw the line between a class 1 and a class 2 residue must also be decided by local conditions.

Sal of
zinc
sulphate

A residue in class 2 is one that contains lead as the only value of consequence in deciding the method of treatment. A residue of this class may be treated in a lead blast furnace, in an ash-fusion gas producer, by the Waelz process, or by various wet methods. The location of the zinc plant with respect to an established lead-smelting plant, the desirability of the particular residue as a feed to the lead plant, and other local conditions will decide the most economical method of treatment.

Leaching with a saturated solution of common salt will recover over 90 per cent of the lead from a residue containing 10 to 12 per cent lead, but will give a comparatively low recovery of silver. Only a short leaching period is required, the leach settles rapidly, and the solution is clear enough to electrolyze without further clarification. Lead is electrolyzed with iron anodes and cathodes; the iron consumption amounts to 0.3 lb. per pound of lead produced. From 12 to 15 lb. of lead is produced per kilowatt-hour. The deposited lead is very spongy and contains about 80 per cent lead when dried. The spongy lead forms a large amount of dross since it oxidizes rapidly in contact with air. The process is really one of concentration rather than a direct reduction of lead, but the low cost of equipment and the high recovery of lead makes this method very attractive for this class of material.

The residue in class 3 is one in which other metals besides lead are present in considerable amounts, but in which lead is in excess of copper in value. The treatment of a residue in this class is usually a straight lead-smelting operation. The low recovery of copper, silver, and gold eliminates the simple brine leach except under especially unfavorable conditions for lead smelting. A considerable amount of work has been done to develop wet methods for the extraction of values from class 3 residues. Several of these wet methods have been tested, but in practically all cases they have been discarded in favor of other methods of treatment. The Waelz process, the ash-fusion gas-producer process, and the electrothermic process are applicable to the treatment of the residue in this class.

Some residue that will fall into class 3 contains scarcely enough lead to pay the freight and the cost of treatment at a lead smelter, but does contain enough silver, gold, and copper to make it a valuable product. Such a residue may be smelted in a reverberatory furnace, with suitable fluxes and reducing material, and a copper matte produced that contains most of the silver and gold. The fume from this furnace will contain a high percentage of lead. This lead can be recovered in a lead smelter. The matte can then be treated in a converter to recover copper, gold, and silver as in the regular production of blister copper. Some lead is reduced to the metallic state in the reverberatory furnace and leaves the furnace with the copper matte. This lead, if in a considerable amount, may be either separated from the matte, or collected as a fume from the converter. The zinc in the residue treated in the reverberatory furnace is largely absorbed by the reverberatory slag, but some is collected with the lead fume. Copper concentrate, or some other sulphur-bearing material for matte formation, limestone, crushed coal, and siliceous ore (if silica is needed) are mixed with the residue to make up the reverberatory charge. Slag containing 30 per cent SiO_2 , 30 per cent FeO , and 16 per cent CaO has been found to carry the least lead and copper and to absorb the most zinc of any of a series covering a wide variation of analyses. Such a slag will normally contain less than 2 per cent lead and over 12 per cent ZnO when treating a residue containing 12 per cent lead and 12 per cent zinc. The amount of screened coal required in the charge is about 4 per cent of the weight of the residue.

A residue in class 4 is one in which the value of the recoverable copper in the residue exceeds that of the lead. Such a residue may be treated in a reverberatory furnace as just described. If the amount of lead in the residue is not high enough to justify the formation of a type of slag to ensure its elimination and the collection of the lead

as fume, the residue may then be advantageously treated in a copper blast furnace or copper reverberatory.

A combination reverberatory and lead blast-furnace method of treatment is especially well adapted to the treatment of residue containing some copper, an appreciable amount of zinc, and not enough lead to make a direct lead blast-furnace treatment economically feasible. Part of the residue may be smelted in a reverberatory furnace and the copper and most of the zinc eliminated in the matte and slag. The fume from this operation, high in lead and low in zinc and copper, can then be added to the remainder of the residue to make up a blast-furnace charge. In this manner the amount of zinc to be slagged in the blast-furnace operation is materially lowered, which reduces the amount of slag formed, and the percentage of lead recovered is greater.

Before zinc-plant residue can be treated in a blast furnace, some form of agglomeration must be resorted to, or the dusting losses will be prohibitive. A fair sinter may be made by mixing the residue with foul slag and coal and putting the mixture over a Dwight-Lloyd machine. It may also be formed into briquettes, without the addition of any other material, which are hard enough so that they may be handled without producing much dust. Fume added to the residue hardens the briquettes, and this additional hardness may be found advantageous if the residue is treated by the combination reverberatory and blast-furnace method. The briquettes may be formed by feeding partly dried residue into a pugmill where just the right amount of water is added to produce a mixture of the proper consistency. This product is then put through an auger brick machine and the resulting ribbon cut into blocks of suitable size. These blocks are then dried. The zinc sulphate and gelatinous material contained in the residue give the material sufficient binding properties to make a good hard briquette.

It is possible to eliminate zinc as a fume, in the reverberatory furnace, but the cost of treatment and the cost of subsequent purification of the solution produced from such a fume is high enough to offset the value of the zinc recovered. Arsenic, antimony, etc., are carried with the zinc fume, and when the fume is leached the solution is so impure that special methods must be used to prepare it for electrolysis.

The Waelz process is a relatively cheap method for the concentration of zinc from low-grade material and is used extensively all over the world. The Waelz process is especially adaptable to the recovery of metals from zinc-plant residues of all classes containing enough values to pay for the cost of treatment. The object of the process is to drive off zinc, lead, and other easily volatilized metals and to concentrate them as a fume. This fume is then treated for recovery of these metals. The kiln residue contains the nonvolatilizable metals and, if sufficient values are present, can be treated for their recovery.

The Waelz process requires no preliminary drying of the residue as slimes containing as high as 40 per cent moisture can be easily treated. The feed is simply mixed with the required amount of coke and fed to the kiln. Almost any sort of coke can be used. The charge is weighed and mixed in any simple sort of mixing machine and fed to the kiln through an inclined chute.

The kiln is a long, horizontally inclined cylinder with a brick-lined steel shell supported on riding rings and rollers. The usual slope of the inclined cylinder is 1 to 6 per cent of the length of the kiln. The kiln is rotated by a pinion driving a large toothed gear fastened around the circumference of the shell. A variable-speed motor is preferred on the larger installations. Some sort of stand-by equipment should be provided to operate the kiln in case the usual source of power fails.

The kiln is fired at the lower or discharge end of the inclined cylinder, and the waste gases are carried away at the feed end. The normal operating temperature

of the kiln is 1100 to 1200°C. at the fire end, and 500 to 600°C. at the exit point of the gases. The kiln is normally operated under induced draft produced by a fan in the collecting system.

The material to be treated is introduced through a chute at the upper end of the inclined cylinder. The rotating motion of the kiln causes the charge to be carried part way up the side of the cylinder in the direction of rotation. From this point it tumbles back into the trough at the bottom. The tumbling action of the charge, together with the incline of the cylinder, causes the charge to work its way slowly down the length of the kiln to the discharge end. The charge moves in a direction opposite to the gas flow. The moisture is evaporated, and the charge absorbs heat both from intimate contact with the hot gases and from contact with the heated lining. The maximum temperature allowable in the kiln is the softening point of the material treated. If the charge softens and begins to slag, all reactions stop immediately. The success of the Waelz process depends on the long period of reduction and on the fact that the reducing and oxidizing zones are actually superimposed on each other throughout the greater part of the kiln.

The fume and dust carried away from the kiln by the hot gases pass through settling chambers and collectors where the dust is settled out. The dust is much heavier than the fume and can be efficiently separated from it. The dust is usually returned to the kiln along with the regular charge. The fume and hot gases are lowered in temperature by passing them through cooling pipes, and the fume is collected in a baghouse or a Cottrell precipitator.

The kiln residue is discharged into any suitable container and is disposed of according to the value of the recoverable metal.

The treatment of zinc-plant residue by the ash-fusion gas-producer method was developed by the Société des Houillères de Saint-Etienne. It has been in use for several years by the Viviez works of the Société de la Vieille-Montagne. The Viviez electrolytic-zinc plant is too far from a lead smelter to make it possible to treat the residue economically by a lead-furnace operation.

The zinc-plant residue as delivered from the filters is first dried to about 5 to 6 per cent moisture in a rotary drier. The product from the drier is slightly moistened with water in a mixing machine and briquetted. The briquettes are further dried to produce a hard firm surface that can be handled without excessive mechanical loss.

The briquettes are added to the furnace along with salt cake and the various necessary fluxes. The slag formed contains about 30 to 34 per cent SiO_2 , 18 to 24 per cent CaO , and 18 to 20 per cent FeO . A slag of this composition will contain a maximum amount of iron with a minimum amount of zinc. The matte produced by this process contains some of the iron and most of the copper, silver, and gold in the original residue. Certain other elements such as cobalt, nickel, manganese, arsenic, and antimony are also eliminated with the matte.

The gas produced by the apparatus carries off the volatilizable metals as a fume. A considerable amount of fine dust also accompanies the flue gases and is collected separately from the fume. The fume is cooled and collected by standard methods and is returned to the electrolytic cycle.

Recovery of Zinc from Lead Blast-furnace Slag.—Zinc can be recovered from lead blast-furnace slag by suitable treatment in a reduction furnace from which the zinc is collected as a fume. The method used at the East Helena slag-treating plant of the Anaconda Copper Mining Co., and elsewhere, has an advantage over most previous methods in that it is able to treat the molten slag direct from the blast furnaces, thereby saving the cost of remelting. It has the further advantage of being able to melt cold slag more cheaply than by treating back through a blast furnace, as pul-

verized coal is used for heating, and the melting and reduction processes are carried on almost simultaneously in the same furnace.

The plant consists of a slag-treating furnace, steel pipes for cooling the fume and gases, and a baghouse for collecting the fume. The furnace is rectangular in cross section, the sides, ends, and top of the furnace are jacketed for water-cooling, and the furnace bottom is a water-cooled cast-iron plate resting on a concrete foundation. Air and coal dust are admitted through tuyères along each side of the furnace, the slag is introduced into the furnace through a charge hole in one end, and the gases and fume are taken off from the opposite end of the furnace. The hot gases and fume are cooled by passing through steel cooling pipes and are filtered through woolen bags in the baghouse for recovery of the fume. The fume collects in hoppers underneath the bags and is drawn from the hoppers into railroad cars for shipment to the electrolytic-zinc plant at Great Falls.

A furnace charge consists of approximately 35 tons of slag. Slag, containing about 10 per cent zinc, is brought to the furnace in pots and is charged into the furnace by raising the pots by a crane and pouring the contents through the charge hole. Blowing is started, and more molten slag and crushed slag skulls are added until the full charge is in the furnace. The percentage of skulls used will vary with operating conditions of the lead blast furnaces, but normally does not exceed 30 per cent of the slag treated. If sufficient molten slag is available, no skulls are treated.

With all molten slag, a furnace cycle is about 30 min. for charging and 140 min. for blowing and discharging. Eight or nine charges can be treated per 24 hr. When skulls or cold slag are treated, the cycle is increased by lengthening the charging and melting period, while the blowing time remains nearly constant.

The zinc elimination is slow until the temperature of the charge has been brought up to around 1050 to 1100°C. After reaching the required temperature, the elimination of zinc proceeds at a fairly constant rate until the zinc content of the slag is reduced to about 3 per cent, when there is a marked slowing down in the rate of reduction. From 80 to 85 per cent elimination of zinc in the slag can be obtained within a 2-hr. blowing period, but this elimination may be increased to over 90 per cent by a longer blowing time. This, however, requires an excessive amount of coal for the amount of zinc eliminated and also reduces the capacity of the furnace. The most efficient period of blowing and the percentage of zinc recovery are determined by the operating conditions and by the value of the zinc recovered.

The consumption of coal in the slag-treating furnace varies from 20 to 30 per cent of the weight of the slag treated when 10,000 B.t.u. coal is used. Air consumption averages about 8000 cu. ft. of free air per minute and is introduced into the furnace under a pressure of 14 lb. per sq. in. Most of the fume comes off during the early part of the blowing period. Fume produced at East Helena averages about 70 per cent zinc and 6 to 7 per cent lead.

CHAPTER XV

PYROMETALLURGY OF ZINC¹BY W. R. INGALLS²

Scope of Chapter.—My contribution to the first edition of "Handbook of Non-ferrous Metallurgy" edited by D. M. Liddell was written in 1925, which was just prior to the general introduction of the process of preferential, or selective, flotation, which by fine grinding made it possible to separate the constituent minerals of almost any kind of mixed sulphide ore, resulting in the liquidation of many great ore deposits previously not of commercial value and bringing to the metallurgists great supplies of very fine ore (so fine as to pass a 200-mesh screen) and introducing new problems in metallurgical treatment. Furthermore, the efficiency of the flotation process was so improved that the grade of the concentrates was raised to upward of 50 per cent in zinc content, with less than 2.5 per cent in lead content, so that the zinc metallurgists were no longer much concerned over lead recovery, deleading having then been done in the mills, where it could be done more efficiently than in the metallurgical works.

The metallurgical problems were solved by the introduction of improved methods of handling, dust catching, and roasting, more particularly desulphurization, in which the introduction of the sintering process played an important part.

The zinc smelters were thus constrained to modernize their plants in these ways, at great cost. Soon, following such modernization, came the introduction of the New Jersey Zinc Co.'s process of distilling continuously in vertical retorts and the continuous electrothermic process of the St. Joseph Lead Co.

Further innovations were the process of refining crude spelter by fractional distillation, invented and introduced by the New Jersey Zinc Co., enabling the distiller to produce zinc of 0.9999 fineness, which was required in the die-casting industry that had been growing by leaps and bounds, and which had previously been supplied by the electrolytic zinc producers by superrefining of their solutions and the use of silver-lead anodes. Another innovation in practice, although it was not new in conception, was the more general dezinking of slags and retort residues by burning the zinc out of them either by the Waelz furnace or otherwise and returning the zinc oxide fume to further processing, which made possible nearly 100 per cent extraction of the zinc from most ores, although of course at additional cost.

Since 1925, the old process of intermittent zinc distillation has survived by virtue of improvements, but there has been no new plant of this type built, except Dumas in Texas. The zinc-distilling plants of the United States using natural gas as fuel have survived, contrary to expectations 15 years ago, but their fuel cost has increased. Additional zinc-smelting capacity during the last 15 years has been either through the continuous-distilling process, or more importantly through further extension of the use of the electrolytic process. The latter has been introduced in places as remote as Broken Hill in Northern Rhodesia, at Flin Flon in Manitoba, and at Cerro de

¹ This paper is a revision of the author's contribution to the Rocky Mountain volume of the American Institute of Mining and Metallurgical Engineers.

² Consulting engineer, New York.

Pasco, high in the Andes of Peru, under conditions where beneficiation by reduction and distilling would be unimaginable. At the present time, we do not foresee further extension of the old process of zinc smelting, although we contemplate its survival.

In view of these radical changes in the art, it appeared best not to undertake to revise the contribution of 1925, but rather to make use of my paper under the title of Intermittent Zinc Distilling from Ore that was published in the Rocky Mountain volume of the American Institute of Mining and Metallurgical Engineers. The privilege of free use of this copyrighted article was generously granted by the A.I.M.E.

The article is now condensed somewhat and also amended it in such ways as have been necessary to bring it up to date. Moreover, the sections on continuous distilling and the processes broader in scope and defined as zinc burning are new.

Some of the preliminary sections describing the travel of zinc ore up to and through the processes of desulphurization of course apply to the whole range of zinc pyrometallurgy and also of its electrometallurgy.

Unloading and Handling Concentrates.—The millman de-waters the flotation concentrate as much as possible, especially to save freight, but it comes to the metallurgist as a stiff mud containing about 10 per cent water. In winter it may freeze in the railway cars, which may have to be passed through a thaw house in order to permit unloading. This may increase materially the cost of unloading as an annual average. In the Middle West a brick house accommodating two box cars will thaw their contents in 24 hr. with the use of 3000 lb. of coal. Under prewar conditions, unloading by hand cost about 12 to 13 cents per ton; it was reduced to 6c. by mechanical unloaders, and raised to 40c. when the ore came frozen, which in a year might be to the extent of 10 per cent.

Ore Storage.—Zinc metallurgists who operate plants in close proximity to their ore supply, especially if the latter is a single mine, require less storage capacity than those situated remotely from the ore supply, and especially those who receive ores from many sources. The arrangements for unloading ore, storing it, etc., are not essentially different from those obtaining in the metallurgy of copper and lead. Whenever the desirability of a mixture is indicated, it is generally accomplished by drawing from separate bins.

Drying.—Flotation concentrates, arriving with about 10 per cent moisture, have to be dried and screened, and perhaps comminuted to break up lumps. In American practice revolving cylinders, internally heated, are used for drying. Plate driers of the Lowden type are also used. For screening, the vibrating sieve is used. Dust loss and other difficulties are obviated if the drying is performed only to reduce the moisture content to 3 or 4 per cent, in which condition the ore is easily handled, letting the drying be finished by spreading the ore on top of the roasting furnace (see Chaps. II, III, and V).

Roasting.—In American practice the Ropp mechanical furnace continues in use among the zinc smelters of the natural-gas fields. Among the zinc smelters which make sulphuric acid as a by-product there are survivals of the Hegeler furnace. However, in all the modernized plants the roasting is now done with circular furnaces of the McDougall type, such as the Wedge, Herreshoff, Skinner, and Warner-Ingalls. These furnaces are built with hearths of about 20 ft. diameter inside and 7 to 16 hearths in height, the larger of these furnaces roasting as much as 50 tons per day to complete desulphurization (much more than that if the desulphurization is not carried down so far) and delivering gas containing 5 per cent sulphur dioxide.

In Europe, furnaces of the McDougall type are also in use, but in general the European roasting is done in Spirlet (mechanical) and Delplace (hand-raked) furnaces. Their capacities are relatively small, say around 10 tons per day, but their efficiencies in respect to fuel consumption, degree of desulphurization, and richness of sulphurous

gas are high, and they have been well adapted to European conditions, whereas they were unsatisfactory when tried in the United States. However, some of the more recent plants of Germany were implemented with furnaces of the McDougall type.

Except for survivals of old construction, muffle furnaces have passed out of use in connection with blende roasting for sulphuric acid manufacture. The control of the gases from furnaces of the McDougall type is so good that they go directly to the Glover towers without need for dispersing separately the combustion gas from carbonaceous fuel.

With most of the modern roasting furnaces, coal consumption ranges from 20 to 10 per cent of the weight of the raw ore, varying according to the type of furnace and the quality of the coal. The best practice is nearer the lower figure than the higher. Instead of coal, natural gas or petroleum may be used. With petroleum as fuel, roasting may be done with 12 gal. per ton of ore, which would be equivalent to about 180 lb. of coal, or 9 per cent. For the purpose of enriching the gas in sulphur dioxide and increasing production of sulphuric acid, brimstone is sometimes burned as a booster and plays the part of a fuel. The brimstone may be burned in a kiln feeding its gas into the ore roaster, or it may be burned in the roaster itself.

Most of the several furnaces of the McDougall type differ only in details such as design of the rabblers and rabbling arms, their attachment to the central column, and the slope of the hearths. The Warner-Ingalls furnace is distinguished by having walls 18 in. thick, flat horizontal hearths, complete circulation of the cooling air through the rabbling arms, introduction of the cooling air at the top of the shaft and discharge of it at the bottom (which is the reverse of the ordinary), transfer of the hot air from the cooling arms through pipes into the four lower hearths, and feeding the ore through vertical drop pipes to a series of hearths in stages. Through these means for the conservation of heat, blende may be dead-roasted without the use of any extraneous fuel.

In all the modernized furnaces of the McDougall type, a great deal of the efficiency is realized from the burning of the ore as it showers from one hearth to the hearth next below. This idea was further developed at Trail, B.C., by taking out the hearths of the Wedge furnace between the uppermost and the bottom and letting the ore shower down. This is now described as shower roasting or flash roasting. It has the advantages of immensely increasing capacity, eliminating the costly maintenance of stirring mechanism, and otherwise reducing costs. These advantages are penalized by a large escape of dust from the furnace with the necessity for providing enlarged means for its collection and re-treatment.

At Avonmouth, in Great Britain, desulphurization is accomplished by making repeated passes of raw ore over a very large sintering machine.

In modern zinc metallurgical practice, blende roasting is done with the furnaces and adaptations of them already described. Many of the varieties of roasting furnaces formerly described are now obsolete, although survivals are still to be found in use in the older plants. The important thing is that blende roasting has been made autogenous, *i.e.*, the heat of desulphurization is caused to do the work, and even with realization of a surplus of heat that may be utilized otherwise.

The modern furnaces of the McDougall type are economical of labor and fuel, but require considerable cast iron and ferrochrome in the upkeep and replacement of their stirring arms and rabblers. In dead-roasting for subsequent zinc distillation, the use of iron and ferroalloy may be as much as 1 lb. per ton of ore roasted, about half as cast iron and half as ferrochrome. Operating labor may be 0.16 to 0.22 man-days and use of power, 13 to 15 kw.-hr. In roasting as a preliminary to electrolytic extraction, the temperature is lower and the requirements for iron are less. In a record of 100,000 tons of ore roasted, the use of cast iron per ton of ore was 0.33 lb.

and of ferrochrome only 0.026 lb. In shower roasting all these quotients are reduced at the expense of increased cost of dust collecting.

Sintering.—In the majority of plants treating sulphide concentrates, both in Europe and America, the ore is sintered preliminary to distilling. This is done for the sake of better desulphurization, which may be carried as low as 0.25 per cent sulphur, and for the sake of improved results in distilling, which follow principally from (1) the better desulphurization and (2) betterment of reduction. This improvement may have been of the order of 4 per cent; *i.e.*, recovery of zinc may be raised from 86 to 90 per cent with reference to the same ore and same practice. However, this is not to be interpreted as a broad generalization; for a plant that was already enjoying good roasting would naturally experience less improvement by virtue of sulphur elimination than a plant in which the roasting was not so good. In general, we had confirmation of the classic theory that one unit of sulphur holds back two units of zinc.

On the other hand, the introduction of sintering carried with it some penalties. It introduced another process, involving the use of heavy machinery requiring attention, power for driving, and upkeep. It introduced also a new outlet through which zinc might escape. However, the total loss of zinc in roasting plus sintering may be as low as 0.5 per cent. In general, it will probably be somewhat higher than that.

In sintering there are two major practices of general use, and two more that are of special use, *i.e.*, employed in single plants or by single operators. The major processes are the original Rigg method, in which the ore is pre-roasted down to about 9 to 10 per cent sulphur and is then sintered. In the United States this is used only at Bartlesville. The other process is the Baelen method, in which the ore is dead-roasted, or nearly so, and then is sintered with admixture of 4 to 6 per cent carbon.

In both these processes the gas that is drawn off from the wind boxes was originally so low in sulphur dioxide as to be useless for manufacture of sulphuric acid, and with the Rigg method there was consequently a considerable loss of sulphur. At Avonmouth, however, by the use of a special seal (1928) covering the joint between the pallets and the wind boxes, dilution was reduced and gas of sufficiently good strength for sulphuric acid manufacture was obtained. This was improved elsewhere by making the pallets slide on a well-greased track, mechanically oiled.

The two special processes are those that are used at Avonmouth and at Overpelt. At Avonmouth, raw ore is desulphurized and sintered by repeated passes, to which reference has been made herein under Roasting.

In the Overpelt process the ore is pre-roasted down to 5 to 7 per cent sulphur and is then moistened with water to which a small proportion of ferrous sulphate is added. The mixture is kneaded and extruded as threads about 4 mm. in diameter and 20 mm. long. After drying, these threads are delivered to the sintering machine, which is able to take a bed about 20 in. deep—manifestly much more than can be charged with fine ore. The purpose of the Overpelt process is obviously to increase the porosity of the bed. The sintering is so expedited that the production of 213 lb. of sinter per square foot of useful grate area per hour is realized. Desulphurization is carried to less than 1 per cent total sulphur, and a gas containing 5 to 5.5 per cent sulphur dioxide is obtained and used for making acid.

In the United States the only sintering apparatus used is the Dwight-Lloyd straight-line machine, which functions like an endless belt, the pallets dumping at one end. In Europe the Dwight-Lloyd straight-line machine is used extensively, but there is also a considerable use of the Schlippenbach, an annular machine, in which the pallets move in a horizontal plane above a ring of wind boxes and trip for their discharge in a blank segment.

There are some differences in control of the operation. Some metallurgists prefer to produce a hard porous sinter, while others prefer a soft friable sinter. This means that in one instance the ore is more extensively fritted than in the other, and of course the nature of the gangue of the ore has a good deal to do with this. There are also differences in practice in respect to the degree of crushing the sintered cakes, the carefulness of sizing, the return of fines, etc. Reduction of cadmium, volatilization, and loss of it obviously occur. By the addition of salt to the charge, lead may be chloridized and volatilized, the ore being thus purified. Such modifications have been the subjects of patents. Reference may be made to the following chapter on Cadmium, page 469.

Dust Collecting.—In roasting with multiple-hearth furnaces of the McDougall type the escape of dust attains large proportions, and with flotation concentrates it may rise to 8 to 10 per cent of the weight of the raw ore charged. The dusty gas escaping from the furnace is commonly led through a brick chamber in which a good deal of the dust, perhaps 50 per cent, settles by gravity, and thence through a Cottrell precipitator designed for hot gas; for of course the clarified gas must reach the Glover tower at a temperature high enough for it to function properly for sulphuric acid manufacture.

In a few plants, dust collection is effected by means of improved Siroccos, which are highly efficient as dust collectors from cool gas but in the course of time operate with impaired efficiency on hot gas containing lead fume. Nevertheless, chamber acid has been made successfully with no other means of dust removal.

In roasting a blende containing cadmium and lead, a large part of the former and a considerable part of the latter are volatilized and recaptured in dust and fume. In roasting an ore containing 0.25 per cent cadmium, the cadmium may commonly be recaptured in the flue dust up to a tenor of 4 per cent, all of it as water-soluble sulphate. Lead is precipitated in the Cottrell fume as sulphate. These products may become sources of cadmium and lead, respectively, as by-products.

Conveying, Cooling, and Mixing.—The calcines discharged from the roasters are conveyed away mechanically by closed conveyers, good forms of which are the Jacoby, the well-known endless-screw, and the push-plate. The calcines may be discharged into a cooler, a long cylinder revolving in a tank of water, in which their temperature may be so reduced that they may be safely dumped into the bins or tanks from which the sintering plant is fed. Up to, and through, the sintering plant all operations are performed in enclosures within which dust is confined or from which escaping dust may be recaptured.

The calcined or sintered ore, crushed and screened, is mixed with the desired proportion of reducing carbon and perhaps the addition of about 1 per cent of sodium chloride. The function of the latter and the practice in respect of it will be discussed later. For reducing coal a good many materials are employed, largely according to availability and cost, *e.g.*, anthracite fines or duff, coke breeze, a mixture of coke breeze and slack coal. Major considerations are not to have too much volatile matter, the minimum of ash, and the minimum of sulphur. As a reducing agent there is some difference in the activity of certain carbons. Charcoal would theoretically be the best.

Reducing coal performs the double function of reducing zinc oxide and also acting as a sponge to hold up molten slags and so protect the retorts. In most American works, the amount of reducing coal used is now 30 per cent or less. It used to be as high as 45 per cent or more. In speaking of these percentages, we always mean the wet weight of the material rather than the dry weight of its carbon.

The mixing is done mechanically, in substantially the same way as the mixing of concrete. The same type of machine is employed for both. In American practice

the mixture is deposited in cars that are trammed to the furnaces, from which it is shoveled directly into the retorts. In some European practice the charge is deposited on the floor immediately in front of the furnace, and if blue powder and other between products are going to be mixed with it that is about the only way to proceed. With mechanical mixing the responsibility of the mix-room foreman is great, for thorough mixing is important. Even after that has been accomplished there is the possibility of re-segregation in subsequent handling, considering that the mixture is composed of materials of quite different specific gravity.

Distilling.—In general practice all over the world distilling is performed in a cycle of 24 hr., of which the maneuver (the operations of drawing spent residue, scraping of condensers, recharging, replacing condensers, replacing broken retorts, etc.) occupies 5 to 2 hr., the latter being exceptionally low, and 4 hr. being about the lowest of good practice in general. After gas has been turned on, about 2 hr. is required for the performance of preliminary reactions, following which the condenser flames become purple and then begin to show tinges of green from burning zinc. The time of active distillation is therefore about 18 hr.; the first quarter is a waxing period and the last quarter is a waning period. Manifestly, the greater the celerity of performing the maneuver, the longer is the period of active distilling, but of course the temperature gradient is an important correlative factor in all this. The cycle might be prolonged from 24 hr. to 30, 32, 36, or 48, and improved recovery with less breakage of retorts may be obtained, but with some increase in costs and with ingenuity in the arrangement of human attention. All these cycles have been tried tentatively, especially in plants in Oklahoma, and at present at least two plants are operated on a 48-hr. cycle.

The smelteries of Oklahoma operating on a 48-hr. cycle have raised their percentage of zinc extraction from about 90 to about 94, computed on the basis of the zinc content of sintered ore entering into the charge for distilling. This improvement is accomplished at some increase in cost for labor and fuel, but not so much as to prevent a net gain from the operation. The improvement in zinc recovery is ascribable to better condensation, resulting from the slower and more regular delivery of zinc vapor from the retort, thus ameliorating the bad proportions between retorts and condensers that are inherent in the American type of Belgian furnace and also the absence of prolongs, the use of which our labor conditions do not permit. The cost of fuel per ton of ore increases only moderately, owing to the lower furnace temperature. Gas per ton of ore for 48 hr. is about 1.3 times what it is for 24. The cost of labor also increases only moderately, because in the intervals between the maneuvers (every other day), there is on duty only a metal drawer, and in firing with natural gas (as in Oklahoma) the labor of attending to furnace temperature is but slight. Finally, if a plant has a surplus of furnaces, its capacity is not diminished by using them in this way. Except under such special conditions, the 48-hr. cycle does not appear to commend itself.

Furnaces.—With but few exceptions the zinc-distilling furnaces of the world are now gas-fired and heat-recuperative in one way or another. Gas is derived from gazogenes, which are installed in batteries near the furnaces, or perhaps in a central plant from which it is piped to all furnaces. The gazogenes, or producers, themselves are of standard types, and as they are employed in great variety they need not be described here, nor even mentioned. Palmerton to a considerable extent employs gas from its spiegeleisen blast furnaces, and Rosita has used coke-oven gas, both of which come to the same thing as a central plant. In the American Southwest, natural gas is employed. Distilling furnaces have been fired with petroleum and with coal dust, but those have not been common practices and are of interest only as precedents.

Pb
Re: Mexico

Coal
Reduction
to Zn et al

Except for our American natural-gas-fired furnaces, almost all distilling furnaces are heat recuperative, indirectly if not directly. The Hegeler furnaces of the United States deliver their products of combustion through waste-heat boilers for generating the steam required in the plant, and the credit for that reduces the furnace quotient to a reasonable figure, perhaps as low as 1 ton of coal per ton of ore. The steam generation is usually short of the plant requirement for power and may have to be boosted by accessory coal-dust firing. Steam boilers may follow regenerative furnaces, but that is unusual and ought not to be necessary if the checkerworks are of adequate capacity, which is not always true. Of the truly recuperative furnaces, the continuous countercurrent system has surrendered to the alternating reversing, or Siemens, system.

Of the reversing regenerative furnaces there are several major types, but their number is not large in respect to differences of principle. In one major type there are four checkerworks, two for air and two for gas. In another major type there are only two checkerworks, which are only for preheating air, and the gas producers are then preferentially put close to their furnace so as to deliver the gas with as much as possible of its initial heat. On the basis of these fundamental differences, furnaces will be distinguished according to the movement of the gas currents within their combustion chambers.

The original Siemens furnace (known as the Auby furnace) has four checkerworks, and the gas and air issuing from their ports rise and descend alternately over a middle wall. Furnaces of this type are used at Rose Lake (Fairmont City) and Palmerton in the United States; at Stolberg (Birkengang works) and elsewhere in Europe; indeed, quite generally in Germany. The Welzer furnace has four checkerworks, from which the gas and air reverse in alternate directions. This furnace is used at Overpelt and Lommel, in Belgium, at Uethemannhuetten in Upper Silesia, and elsewhere. The Tanier furnace that was developed at Sclaigieux is a modification of the Welzer and is used extensively at other plants in Belgium and in the north of France. The Van Gulck furnace has checkerworks for preheating air only. The gas and air reverse over a middle wall, as in the Auby furnace. The Van Gulck furnace is used at Avonmouth and at Swansea and formerly at Mortagne.

The Dor-Delattre furnace, which was developed at Budel, also has checkerworks only for preheating air. It is distinguished from all other distilling furnaces. Instead of having the checkerworks in the inferior structure, the Dor-Delattre has them at the end of the superior structure and conveys the gas and air through longitudinal canals above the combustion chamber instead of beneath it. In the Berzelius works at Duisburg the furnaces are of similar design. Asturienne has Dor-Delattre furnaces at Auby and at Aviles (Spain), and when Vieille Montagne rebuilt Flône and Valentin Cocq it adopted this form of furnace. The Dor-Delattre design permits the checkerworks to be built of adequate capacity, only at the expense of floor space; whereas when they are built in the lower part of the furnace, they are subject to certain limitations and frequently are not made large enough. The Dor-Delattre system may have some other advantages.

Except the Dor-Delattre furnace, all the regenerative distilling furnaces have their checkerworks in their substructure. As to their superstructure it is now difficult to classify sharply between the Belgian and the Rhenish type, for whereas some furnaces exist in their purity, there are many that share the characteristics of both types. The Rhenish furnaces of Europe have commonly 216 to 288 retorts of 2 to 3 cu. ft. internal volume, arranged in three rows, the two fronts being divided into closets, each containing the condensers of two retorts. The Belgian furnace has retorts of smaller volume, say 1.5 to 2.2 cu. ft., and more of them; the Dor-Delattre has 432, arranged in six rows, but five-row furnaces are more common. In the United States

our Hegeler furnaces have commonly 608 retorts in four rows. The Neureuther-Siemens furnaces have commonly 800 retorts in five rows. In general, the tendency in the United States has been to reduce the number of rows to four, especially in the Hegeler and natural-gas-fired furnaces. American metallurgists generally stick to the cylindrical retort, but some have adopted retorts of elliptical cross section, and in certain instances their axes are as large as those of the Rhenish retort. In all American furnaces the inner ends of the retorts rest on ledges projecting from the middle wall. Such construction also obtains extensively in Europe, but with the pure Rhenish furnaces there is no middle wall, the arch springing from face to face, while the inner ends of the retorts rest on the ledges of a perforated wall or banquette, which with retorts of great length, up to 72 in., and even 78 in., when an intermediate support of the same nature is provided. In American practice, retorts longer than 54 in. are seldom to be observed, although we do go up to 60 in.

Even with the purely Belgian furnaces the *devanture* (the front structure) is deeper in Belgium than in America, *i.e.*, the condensers do not stick out so far beyond the plane of the face of the furnace. The Dor-Delattre furnace has a shield that can be pulled up or down, more or less like a Venetian blind, protecting the front of the furnace against drafts of air. The same thing was in the mind of E. C. Hegeler when he surrounded his entire furnace with a curtain of sheet iron, which also is to be seen at Danville. The Rhenish furnaces usually have hoods extending along each front of the furnace, connecting with a main, through which noxious gas and fume are drawn off. Escaping zinc oxide, chloride, etc., may be recovered from this system, but trials in the way of doing so have demonstrated that it is not worth while. The prolongs themselves are effective collectors. From a European zinc distillery there does not hang the great cloud of white smoke that hovers over many American plants.

The essential requirements of a distilling furnace are economy of fuel, uniformity of temperature, and such arrangement of inlets and outlets for gas, air, and combustion products that they do not become clogged with dripping slag, dust, etc. Economy of fuel results from the proper proportion of retort space to combustion chamber, and of checkerworks, together with avoidance of excess of secondary air. Uniformity of temperature is accomplished by the proper distribution of combustion and restriction of the alternating travel of the burning gas. In any reversing regenerative furnace, whether the currents are up and down, down and up, or end to end, there will be a neutral zone midway, where the furnace temperature will be slightly inferior. In the old Siemens furnace this zone will be above the middle wall, where there may be a fall of 50°C. in the furnace temperature. The metallurgist aims to achieve an even glow of white heat throughout the combustion chamber. In furnaces of the Welzer type (end-to-end reversal) the neutral zone is probably reduced to the minimum, for the gas and air enter alternately through ports almost up to the median transverse line.

Plant Layout.—Modern zinc-distilling furnaces are built entirely above ground, except for their foundations, and are attended from the upper floor. The residues drop into side pockets, from which they slide into cars to be trammed away. Sometimes a mechanical conveyer is provided for that purpose. American furnaces of the Hegeler type and those in the natural-gas fields still have ash tunnels under them through which residues are removed.

In European plants the furnaces are commonly lined up end to end with the retort-tempering ovens between them, several furnaces being grouped in a hall. Such a layout exists at Palmerton, but elsewhere in the United States the furnaces are laid out in parallel, each in its own house, except in the natural-gas fields, where there are two per house. In the vernacular of those districts, the separate furnaces are called "stoves," a pair of them still being regarded as a "block."

Most zinc-smelting plants having been evolutionary, there are to be observed in them unbalances among functional departments and irregularities in equipment, such as furnaces of different types, different sizes of the same type, and different forms and sizes of retorts in the same furnace. Sometimes metallurgists consider that they have good reasons for variations; i.e., elliptical retorts in the lower three rows and cylindrical in the upper two may be held advantageous for certain furnaces and certain ores. The ideal plant has all functions in balance in multiples of two and all parts alike in each department. Thus, there may be four roasters, four acid systems, two sinterers, and eight distillers, with no bottlenecks among the several departments.

Retorts and Condensers.—The essential features of the process of distilling in the intermittent way are the retorts and condensers, which are made in a separate factory of the plant that in the American vernacular is called the "pottery." From this the retorts, after seasoning (drying), are delivered to the distilling furnaces day by day as required, and after tempering in a near-by kiln, where they are brought slowly up to the bright red heat, or as nearly to furnace temperature as possible, they are drawn out for making replacements in the furnace.

The batch for making retorts is a mixture of burnt clay (chamotte, grog) coarsely crushed and of raw fat clay in proportions of 50:50 to 60:40. The chamotte forms the skeleton of the concrete and the plastic raw clay is the binder. The more chamotte, the stronger is the retort; the more fine clay, the less porous is it. A physical balance has to be struck. There are also chemical considerations insofar as the character and composition of the clays, together with other materials, may be adjusted to the character of the gangue of the ore, from which slags will result. If the gangue is siliceous, the retort should also be strongly siliceous; if the gangue is basic, either from iron or lime or both, the retort should be aluminous or inert.

In accomplishing such purposes, substitutions for parts of the chamotte and clay are made. A common substitution almost everywhere in Europe is the introduction of coke dust, which should be as fine as possible, to the extent of 10 or 15 per cent, but in America this is scarcely ever used. The coke dust tends to give the retort somewhat of the qualities of a graphite crucible. Another substitution is the introduction of some granular quartz, for the purpose of making the retort more siliceous. However, inasmuch as quartz has a higher coefficient of expansion than clay, the grains of it tend to have a rupturing effect when the retort is heated. This is counteracted by adding the silica in the form of flour, which during recent years has been widely adopted in American practice. A mixture might be, for example, 25 per cent chamotte, 25 per cent silica flour, and 50 per cent clay. Such retorts have done very well with siliceous Joplin ore. Another innovation has been the use of carborundum retorts, e.g., 65 per cent carborundum and 35 per cent clay, which has occurred both in Europe and America and has offered the theoretical advantages of better heat conductivity and long life. With the retort of unchanged diameter, other conditions remaining the same, the better conductivity may increase zinc recovery by 2 per cent; or the diameter of the retort may be increased (as at Amarillo and Rosita) and heavier charging may be accomplished with undiminished zinc recovery. The life of the retorts may be tripled. With ferruginous ores and furnaces fired with producer gas, however, ventures with carborundum retorts in some instances have been quite disastrous, the retorts suffering corrosion from the outside as well as from the inside. Naturally, the carborundum retorts are much more costly than the clay retorts. The carborundum retort is therefore a utensil of occasional rather than of general use.

With all types of retorts, it is obvious that the thinner the wall, the better the conductivity. Practice has everywhere for a long time settled on a wall thickness of about 1 in. and a butt thickness of about 2 in. As among the ordinary clay retorts,

the graphitized retort, and the silica-flour retort, there does not seem to be any material difference in conductivity as determined by pyrometric observations or in the way of zinc recovery apart from the matter of breakage.

In cross section and dimensions the retorts that are used at present are of wide variety. The commonest form of the Belgian retort is circular, $7\frac{1}{2}$ to 8 in. in diameter. Extensively used also are retorts of elliptical cross section. While we so describe them, they are really two half-circles joined by a rectangle, which gives them straight sides. Dimensions may range from $6\frac{1}{2}$ to $7\frac{1}{2}$ in. for the short axis (width) and 9 to 12 in. for the long axis (height). As a general principle, reduction in width improves penetration of heat, reduces retention of zinc in the residue, and improves recovery. Height is not a factor in this. Reducing the width of a retort from $8\frac{1}{2}$ to 8 in. brings about a striking improvement, from 8 to $7\frac{1}{2}$ further improvement, but not so strong, from $7\frac{1}{2}$ to 7 and from 7 to $6\frac{1}{2}$ still further improvement, but at diminishing rates. In going below 7 in., there is increased difficulty in charging.

Besides the circular and elliptical cross section there are also the muffle-shaped (not much in use now) and the oblong (with rounded edges), the latter to be much commended. Different forms and dimensions may be produced by simply changing the die of the press.

In length, inside dimensions, retorts run generally from 48 to 72 in. In European practice they are longer than in American, for we seldom go beyond 54 in. The ability to charge well and mechanical strength are of course governing factors. We may consider the retort as a hollow beam, constructed of fragile material, supported at each end and carrying a uniformly distributed load of perhaps 250 lb. at temperature of perhaps 1500°C.

The cross section of the retort and its length compound into cubic measure, or internal volume or capacity. In use in the United States are retorts ranging from 1.5 cu. ft. (old) to 2.2 cu. ft. In Europe in some Rhenish furnaces they are of 3 cu. ft. In general there has been in recent years a tendency to increase volume for the sake of increased charging. Retorts 1.9 m., or 76 in., in length are on record.

In all modern plants the retorts are molded under a pressure of about 150 atm. by means of the Mehler or Dor-Delattre hydraulic presses, which are improvements of the original Dor press. The molded retorts are transferred to the drying rooms, where they season by gradual loss of their water. As freshly molded, they contain 12 to 15 per cent water and are introduced into the drying rooms at a temperature of 60 to 70°F. With a gradual rise in temperature after the first 15 days, their water content will have been reduced to about 2.5 per cent at the end of 30 days, to about 1 per cent at the end of 60 days, and to about 0.3 per cent at the end of 90 days, the temperature being gradually elevated to something like 130°F.

Practice varies in respect to the speed and duration of drying. Some metallurgists use their retorts after a month of drying, while others insist on 3 months, or 4 months, with a slow increase of temperature. There are records of substantial increases in retort life as a consequence of care and patience in this particular. At the best, a retort of clay or other refractory material is an imperfect vessel, being subject to porosity, to microscopic cracks, and to differences in strength when regarded as a beam. Retorts may be tested by closing them with an airtight cover, pumping air into them under pressure, as into an automobile tube, and painting the exterior with a solution of soap. Loss of pressure, which is always rapid, correlates with development of soap bubbles on the exterior, which are uniform if the retort is homogeneous, but irregular if there are microscopic rents, which let the air out very quickly. In order to counteract porosity, the retorts in European practice are commonly dressed inside and out with a slurry of powdered glass and soda, or similar composition which upon burning glazes the retort. Such glazing is seldom done in American practice.

In pugging the mixture of refractory materials and cutting it up into blocks for introduction into the press, care is taken to avoid trapping air or to allow for its escape before pressing. Otherwise, it may be entrained in the molded retort, and may even appear as blisters, impairing the quality of the retort. At Donora, the Wettengel pug mill has been modified by interpolating a vacuum chamber between the compression zone and the extrusion barrel and thus de-aerating. This has been found to increase the mechanical strength of the retort, increase its density, reduce drying time, and increase life in furnace, at an immaterial increase in costs for the power requirements for the vacuum pump.

Condensers are made from mixtures of clay as for retorts, but inferior grades are used, and old retorts, cleaned of slag and crushed, often take the place of chamotte. In the United States, most condensers are of the simple conical form and are made by a machine that forces a conical mandril into a conical mold containing the requisite quantity of clay. A belly may be produced in the tube by cutting out a gore from the larger end and drawing the two sides together, which, of course, is handwork. Condensers have been made by machine molding, with a diameter at the large end that is greater than the interior diameter of the retort to which it is to fit: it is reduced to fit by inverting the molded condenser into a conical ring, which is called "crimping." This produces a bottle-shaped condenser and may increase the interior area from 300 sq. in. to about 360. Many different shapes of condensers have been, and are now, used. The more complicated they become, the more handwork is required. The old Rhenish condenser was a substantially rectangular tube, rounded at the top. The Dagner condenser, used in Upper Silesia, is a composition of rectangular tubes.

In length the Belgian condensers vary from 18 to 24 in., while the Rhenish and Silesian condensers were about 36 in. long. Recently, some of the Belgian metallurgists have increased the length of their condensers, even to as much as 36 in. This subject is complicated and will best be discussed further on when furnace operation is considered.

Condensers are sometimes burned prior to use and sometimes are used unburned. Either way the breakage of them is large, and as will be seen subsequently, this is a very important matter. The breakage is partly mechanical, from careless handling, and partly chemical. The latter is evinced by splits occurring while the condenser is in place and not being handled, such as a longitudinal rent or a ring rent that may let the nose fall off. Specks of iron oxides in the clay and the action of hot carbon monoxide may have something to do with this.

Coal Consumption.—The records are generally not comparable, for they fail to take into account the value of the coal, the grade of the ore, and other variables, among which are both the type of furnace and the proportions of the furnace. The thermal efficiency of the best furnace is so low that large changes in the charging may be made without affecting the quantity of coal burned in the producers, but greatly altering the quotient of pounds of coal per ton of ore. The temperature of the products of combustion escaping from a regenerative furnace to the chimney is not even a true gauge, for though a temperature of 300°C. looks good the volume of the wasting gases may be too high, which it always will be if the excess of secondary air is too great.

Our practical deductions therefore are quite empirical. A Hegeler furnace distilling ore of 70 per cent grade with gas produced from coal of 13,000 B.t.u. may give a figure of 1½ ton per ton of ore, which with a steam credit of one-third may be reduced to 1 ton net. On the same grade of ore a regenerative furnace with coal of 12,000 B.t.u. may give a quotient of 1.1 ton, which perhaps might be reduced by heavier charging. With the best regenerative furnaces and the best practice, coal quotients of 0.9 and 0.8 are rather common. One furnace is known that with coal

of 13,000 B.t.u. used only 0.72 over a month. These figures are very different from those of the old direct-fired furnaces that used to consume 3 or 4 tons of coal per ton of ore. However, when we look at the New Jersey continuous furnace and see quotients like 0.5, we are conscious that we still have some distance to go. We should not overlook that in intermittent distilling there is a period of 6 hr. or so, including the time of the maneuver, when the furnace has to be kept hot without doing any directly useful work, whereof 0.8 ton in one case and 0.5 in the other are not perhaps very much out of harmony.¹ We may also be cognizant that the intermittent furnace, having to rework a large proportion of intermediate products, is required to do the same work twice over.

Reduction and Condensation.—The zinc oxide of some ores reduces more easily than that of other ores. One of the advantages of sintering has been improvement in that respect. The activity of the carbon employed as reducing agent also plays a role. Apart from such differences, the controlling factors in reduction are temperature and time, which are correlative. Time may be increased by shortening the maneuver or extending the cycle to something more than 24 hr. Temperature is limited by the durability of the retorts and the stability of the furnace. In European practice there are maximum temperatures of 1400 to 1500°C.; in American practice, 1300 to 1400°, but rarely as high as the latter. These are temperatures in the combustion chamber; inside a clay retort with a 1-in. wall the temperature will be 100 to 200° lower. The front ends of the retorts, resting on shelves, will not be so hot as further in, consequently there will be poorly reduced ore in that place. Carborundum retorts, because of their superior conductivity, run hotter toward the front than do clay retorts.

When the reduction of zinc begins and the vapor starts to come over, the preliminary reactions have not been fully completed and the gas is high in carbon dioxide, which as the temperature falls in the condenser acts oxidizingly on the droplets of zinc and produces blue powder, from which we are never entirely immune, although in the course of time the gas discharges with only about 1 per cent carbon dioxide. The blue powder, which to the naked eye is merely an impalpable dust, really is composed of microscopic globules, which show frostings and sproutings of zinc oxide that prevent the globules from coalescing. Amelioration of this is the rationale of the addition of about 1 per cent of sodium chloride to the ore. Volatilizing it is intended to dissolve the zinc oxide as chloride or oxychloride and so clean the pellicles of zinc and allow them to melt down. Probably that occurs. Anyway zinc chloride is found in the prolong dust. This spells a loss of zinc, though perhaps no more than will be suffered in redistilling a larger quantity of dust. At all events, the addition of sodium chloride to the ore is not essential and in some practice has been abandoned. In the absence of salt, the condenser flame is of course deprived of the sodium coloration, which is a guide to old-time furnacemen.

The observation may be made that in American practice it is common to "stuff" the condensers, *i.e.*, partly to close their outlet, allowing the gas to escape through a small hole, which is kept open by constant "spiesing." This gives a certain internal pressure in the retort and condenser, and if this becomes too much, through inattention, the gas and vapor may break out through the luting around the joint between condenser and retort. When prolongs are used on the condensers, they are open. If the prolong is on tightly, the gas escapes through only the small hole near its end.

A logical condenser is a long pipe folded in zigzag and enclosed in a closet whose temperature can be controlled, as in the Dagner condenser of the Silesian furnace, but this is not easily applicable to a furnace of more than one row of retorts or to the

¹ In using this illustrative quotient for the continuous furnace, I have in mind data prior to utilization of the gas escaping from the condenser.

practice of daily taking down and putting up. The Belgian and Rhenish furnaces with condensers registering with the retorts are restricted in length by thermal conditions, which is not, perhaps, of great importance inasmuch as lengthening may not add much to internal superficial area; and increase in girth is restricted by lack of room and difficulty in getting at the joint for luting, etc.

As the internal volume of the retort is increased and the density of charging is also increased, there should be a corresponding increase in the capacity of the condensers. With a retort of 1.75 cu. ft., the condenser may have 300 sq. in. of internal surface. With a retort of 2 cu. ft. the internal area of the condenser may be 400 sq. in. The latter is about a practicable limit. These are only rough guides. The correlation between volume of retort and condenser surface is naturally affected by the quantity of zinc that is charged into the retort and the evenness in distilling it.

Charging.—The practice of keeping up the condensers and charging through them by spoon prevailed extensively in Europe until recently, but most works have gone over to the Belgian practices of making a condenser that fits the retort, taking it down and putting it up every day and filling the retort by throwing in the charge.

The charger has one of the very responsible positions. His work is arduous. The idea of substituting mechanical charging for hand charging has consequently been engaging. Numerous mechanical chargers have been designed and applied on a regular working scale. These may be generalized as slingers and shooters, the former being designed to throw in the charge and the latter to shoot it in.

In general, the conclusion has been that with mechanical chargers there is no material gain either in labor saving or in efficiency of performance, and that when first cost, upkeep, etc., are considered, they are not worth while. At Rothem (in Belgium), however, the Dor-Delattre charger, which shoots in the charge, continued in regular use for a good many years. It put 13,000 lb. of ore into 210 retorts in 20 min., and reduced the total time of the maneuver to 2 hr., leaving 22 hr. for distilling.

Density of Charging.—Much attention has been given to increasing the density of the charge, which means increasing the number of pounds of ore introduced per cubic foot of retort volume. Accomplishment of improvement in this direction depends on several factors, among which are (1) the specific gravity of the ore; (2) proportion of reduction material mixed with the ore, for obviously the less reduction material, the more room there will be for the ore; (3) care with which the charge is thrown in, avoiding cavities; and (4) force with which the charge is thrown in. An expert charger can throw a shovelful of charge into the retort with such force as to break its butt. A mechanical charger can put a quantity of ore into a given retort that in comparison with the best hand-charging is almost unbelievable, and can do it so densely that a strong man is unable to drive in the spieß rod. Such excessive density of charging may introduce more zinc into the retort than, after reduction and vaporizing, the condensers are able to handle; therefore recovery of zinc may be impaired rather than improved. Up to this critical point, however, increase in density of charging is beneficial from the standpoint of metallurgical reactions in the same way that a briquetted charge may be beneficial.

In American practice, charging sintered ore weighing about 105 lb. per cu. ft., mixed with 30 per cent of reduction coal, wet weight, about 55 lb. of ore per cu. ft., or 110 lb. in a retort of 2 cu. ft. capacity, is charged; here and there that figure is exceeded.

Furnace Charging.—Although density of charging per retort has a good deal to do with the charging of the furnace as a whole, the subjects are two different things, although this is commonly overlooked, and the two expressions are commonly confused. The zinc that is reduced and vaporized is not wholly condensed directly as spelter. We may get 65 to 70 per cent of it as direct spelter, the remainder as zinc

Dimensions
of
Retort, etc., decrease

dust, blue powder, which must be redistilled. Besides the blue powder that is skimmed from the ladles and recovered from the prolongs, there are other between products that must be redistilled, including the imperfectly distilled ore remaining in the front end, perhaps 10 per cent, of the retort, which in American vernacular is called the "sample" and in the Belgian vernacular is called the *gueules*, or "throats"; the cleanings from the condensers; and the cleanings from the pans on the floor along the front of the furnace. In good practice these collections may aggregate 20 per cent of the weight of the original charge; in careless practice they may run to 30 per cent.

In American practice this entire collection is described as blue powder. With the Hegeler furnaces it is recharged into the sections of retorts at the chimney end of the furnace. With the Siemens furnace it is charged into the uppermost row of the retorts. In Europe it is more generally mixed with the ore. In occasional practice it is reserved and redistilled in a separate furnace. Whatever the method, it occupies furnace room, increases the fuel and labor quotients per ton of ore, and subjects a certain portion of the zinc to a renewed opportunity for loss.

Translated into terms of furnace charging, if a furnace of 600 retorts, or 1200 cu. ft., should be charged fully at the rate of 55 lb. per cu. ft., it would receive 72,000 lb., but if only 480 retorts can be charged with ore the total is 52,800, and if only 420 can be charged with ore the total is 46,200, and all the quotients are altered accordingly. The furnace charging is therefore a composite of the density of charging and the proportion of between products.

These illustrative computations are exclusive of old condensers, which may be crushed and added to the charge or may be crushed and jigged and the concentrate added to the charge; or the concentrate may be accumulated and be distilled separately. All these practices are to be observed.

Losses in Distilling.—In present good practice, distilling sintered ore, the recovery of zinc is 90 per cent plus, exclusive of recovery that may be realized by the use of prolongs and of additional recovery by re-treatment of residues in one or more ways. Equally good recovery is accomplished from ore with iron gangue, or limey, or simple quartz if suitable adjustments are made by the metallurgist.

In considering the subject of zinc recovery, it is important to examine the ways in which loss of zinc occurs in distilling. Most important is its retention in the residue. Apart from that, the losses are scattered: absorption by retorts, retention by condensers, escape from condensers (if prolongs are not used), filtration through retorts and leakage by retorts breaking, contributing to loss up the chimney (which is a loss that is very difficult to measure). There is some recovery of zinc from dust and fume depositing in checkerworks and settling on furnace tops, but both are troublesome.

The loss is aggravated by the exigency of redistilling some between products. For example, we might expect to obtain 70 per cent of the zinc of the ore as spelter and 22.5 per cent as between products divided approximately as follows: in ladle skimmings, 16 per cent; in condenser cleanings, 2.5 per cent; in pan cleanings, 1.5 per cent; in "sample" (or throats), 2.5 per cent; all these being aggregated as "blue powder." Upon redistilling we may get from them 20 per cent (with reference to the ore charge), and the zinc recovery will be 70 per cent + 20 per cent = 90 per cent. The ultimate loss of 10 per cent may then be reckoned approximately as shown in the table on page 458.

The residue may amount to 30 per cent of the ore charged and assay 13 to 14 per cent zinc. Nearly half of its zinc content may be in oxidized form capable of being reduced. Daily loss of condensers was 15 per cent. Each discarded condenser contained about 7 lb. of zinc. By crushing and jigging, about two-thirds of its zinc could be recovered in a concentrate assaying about 70 per cent zinc, of course at a

certain cost. This salvage is not included in the analysis of recovery and loss. The absorption of zinc in retorts is computed on a basis of daily loss of 3.33 per cent (correlating with 30-day life). Each discarded retort carries away about 6 lb. of zinc. The loss of zinc escaping through the chimney is computable only by difference. It is more or less proportionate to the percentage of breaking retorts.

Direct spelter.....	70.0
Blue-powder spelter.....	20.0
Total spelter.....	90.0
Zinc in ore residue.....	3.8
Zinc in blue-powder residue.....	1.2
Zinc retained by condensers.....	2.3
Zinc absorbed in retorts.....	0.5
Zinc escaping from condensers.....	0.5
Zinc escaping through chimney.....	1.8
Total accounting.....	100.0

Many zinc-distilling balance sheets will be more or less in harmony with this. With the use of prolongs, the loss of zinc by escape from the condensers is practically excised. The loss of zinc by absorption in the retort is negligible. Old condensers generally assay about 30 per cent zinc, and the greater the breakage rate, the more do they carry away. Although the larger part of such zinc may be regained, there is additional cost, both for milling and distilling.

With regenerative furnaces there is some recovery of zinc from the checkerworks when they are cleaned. In one plant this averaged 25 per cent zinc by assay and figured to 0.3 per cent of the zinc in the ore charged. Cleaning of the tops of the furnaces also gives a product assaying about 25 per cent zinc and accounting for 0.2 per cent. This dust is used in the mixtures for stuffing and luting condensers, and so finds its way back into the blue powder.

The primary recovery of 92.5 per cent of the zinc that will be reduced to an ultimate recovery of 90 per cent, as already outlined, suggests that something better may be done with the blue powder than redistilling it in the primary furnace, whereof 20 to 30 per cent of its cubic feet of internal volume is occupied for this purpose. This is emphasized if, as in some European practice just prior to the war, the size of the retorts and the density of charging are increased so that no practicable condenser can be attached for the maximum collection of zinc and the only expedient is to increase the collection of zinc as dust in the prolongs. Such collection may exceed ability to market zinc dust. A rational expedient is then to apply the Thede process of rubbing the zinc dust in a heated revolving cylinder so that the cleaned zinc will melt down, this being similar to the Cornelius process used in Sweden (see the sections on Zinc Dust and Electrothermic Smelting at Trollhättan). This illustrates moreover the wide diversity of the factors in intermittent zinc distilling that must be considered and correlated in harmonizing any works practice.

According to Dr. Thede, describing the practice at Muensterbusch, Stolberg, Germany, where his process was introduced, the separate treatment of zinc dust costs only one-tenth as much per pound of spelter produced as redistilling, and with a smaller loss of zinc, so that recovery of zinc on the basis of the content of ore originally charged is raised to 95 per cent. The loss of zinc in the Thede process itself is small and chiefly mechanical. Moreover, by keeping the dust spelter separate the cadmium content of the direct spelter is reduced.

Metal Drawing.—Spelter was drawn from the Silesian and the original Rhenish condensers only once during 24 hr. With the smaller Belgian condensers, more draws

were necessary, and even more as the grade of the ore increased. In American practice, four draws are the common daily routine.

In quantity the draws vary according to the period, correlating with the activity of the distilling. The following is more or less typical of the draws in American practice:

Draw	From calcines, per cent	From sinter, per cent	Time
First.....	23	22.2	2.30 P.M.
Second.....	29	29.4	7.00 P.M.
Third.....	29.6	29.0	12.30 A.M.
Fourth.....	18.4	19.4	6.30 A.M.
Total.....	100.0	100.0	

This introduces the subject of the temperature gradient, or what may be plotted as the furnace thermograph. This is more or less variable according to the operating conditions. Beginning at 1000 to 1050°C. with "gas on" and immediately after completion of the maneuver, it may rise in a straight line, or in a slightly arched line, with different speeds. With a rapid rise the maximum, 1330°C., may be attained at 11.30 P.M. With a slow rise it may not be attained until 2.30 A.M. The rate of reduction naturally correlates with the thermograph. After the maximum has been attained, it is held level for several hours, or until the distilling of zinc is distinctly on the wane, nearing its end, when the temperature is allowed to fall to save retorts from being "butchered" when there is no longer an endothermic reaction occurring within them.

The temperatures suggested here are as registered by Seger cones inside an open retort. It is common practice to record furnace temperatures in that way, and temperatures in the combustion chamber by means of recording pyrometers. Even when the latter are used, however, the Seger cones afford a valuable check.

In European practice the spelter is commonly drawn into small ladles by hand. With some furnaces, the lowest row of retorts is so near the floor that nothing else can be used. In American practice a large kettle carried on a car on the rails in front of the furnace is universally employed. The spelter is drawn directly into this. When the kettle is full, the metal is skimmed and then poured into a row of molds. There is no question as to the superiority of this method.

Retort Residue.—After distilling has been completed, the spent residues must be withdrawn, usually by hand, but machines have been found useful in some plants, without becoming of general application. In some American practice a water pipe is introduced into the retort, letting out a little water, which immediately becomes converted to steam and blows out most of the residues. With the fluffy residues from Joplin ore this system works very well, but with a slaggy or "gummy" residue, it has to be hoed out.

Some lead from a leady ore goes over into the spelter. A considerable proportion of it may be recovered by gravity refining, but that which is retained by the spelter adds to the weight of the latter and realizes the spelter price for good ordinary brands. Most of the lead and all the gold, silver, and copper remain in the residue. If the silver content is high, which has occurred with some ores, the entire residue may be passed on to the lead smelter. In general, however, the residue used to be jigged for separation of its lead, together with the silver carried by it, if that were worth while.

The flotation process has been so effective in deleading ores that there is now but little need for recovery of lead from retort residues, but they are sometimes jigged and washed for recovery of undistilled zinc, unburned coal, etc. It is now a common practice to put retort residues through the Waelz process, burn out unreduced zinc, recover it as fume, and put that back into the charge for distilling.

Labor.—In the management of the zinc-distilling furnace there are two systems: in the one commonly practiced in America, the furnace crew of 30 or so is divided into groups of specialists, each group performing a single operation; in the other, which is in general practice in Europe, the furnace crew, which is always relatively small, is divided into squads, each of which takes charge of the operation of a part of a furnace, a half or a quarter, collectively performing all the operations of the maneuver. After the maneuver has been finished, the furnace passes into the charge of the fireman and the metal drawers, who work in the same way by either system.

An American furnace of 608 retorts was charged with 24 tons (of 2000 lb.) of ore and was attended by a crew of 30 men, inclusive of gas producers but exclusive of those who removed residues from the ash pockets. This figured to 1.25 man-days per ton of ore. Contemporaneously one of the most modern of the gas-fired furnaces in Belgium received a charge of 11 short tons of ore and had a crew of 20 men, which figured to 1.8 man-days per ton of ore. However, the Belgian furnace was operated with prolongs, which the American was not.

These labor quotients are computed on the basis of roasted ore. On the basis of raw ore in a well-mechanized plant in the United States, with furnaces fired with producer gas, the use of labor will hover around 2 man-days per ton of ore.

Refining.—Cadmium and lead both go over with zinc. Cadmium concentrates in the first draw of spelter. Lead is higher in the later draws. Some grading is accomplished by keeping them separate. Drawing into the large kettles in American use, there is some equalization of the molten metal, but even so there may be wide variations in the draws from different parts of the furnace, especially from our Hegeler furnaces that have so pronounced a drop in temperatures.

By remelting the spelter it can be equalized, and the excess of lead settles out. This is the simple process of gravity refining. Refining may also be done by redistilling, but that does not get rid of cadmium. The New Jersey process of reflux refining enables ordinary spelter to be raised to four-nine grade and in this respect puts the old process of intermittent distilling on equal terms with electrolytic refining.

The New Jersey Zinc Co.'s process of refining is a means of integrating in one operation multiple stages of fractional distillation and fractional condensation. The liquid metal and metallic vapor travel countercurrently through a column, the heat for boiling being supplied at the lower end of the column and the heat of condensation removed at the upper end. In practical application, spelter is melted in a pot whence it is introduced into what is called the "lead column," which comprises a series of superimposed trays of refractory material with staggered openings, permitting the liquid metal to cascade downward in intimate contact with metallic vapors ascending countercurrently. From the top of this rectifying column, zinc vapor passes into a condenser whence molten zinc issues into what is called the "cadmium column." From the top of the latter, cadmium is condensed as a dust or otherwise as a cadmium-zinc alloy. From the bottom of the cadmium column, refined zinc is obtained. From the bottom of the lead column, the metal from which the zinc has been mostly boiled off is collected in a liquating pot which gives impure zinc to be recycled and lead and zinc-iron dross separated by gravity.

The columns and their fittings are equipped from suitable refractory material. A refining unit is of 15 tons daily capacity, operating continuously. Prime Western spelter in this country, or g.o.b. metal in Europe, is raised to 99.99+ per cent zinc.

The direct production of this grade is about 96 per cent of the zinc in the feed; of the remaining 4 per cent all but 0.5 to 0.75 per cent is accounted for in the skimmings, dross, and other by-products. In connection with the New Jersey process of continuous distilling, the feed metal is run directly to the refining unit.

The New Jersey refining process is strongly patented and is used in the United States and in a few countries in Europe under licenses.

Zinc Dust.—In the United States there was a prewar production and consumption of about 15,000 tons of zinc dust, also called zinc gray and blue powder, and in Europe a larger quantity. In Europe where prolongs are used in the distilling of ore, the dust from them may be made commercial, and of a quality of 90 per cent zinc unoxidized, by sifting and grading. In general it is difficult otherwise to obtain such a grade directly from ore.

In the United States the prewar specification for prime zinc dust was 96 per cent metallic zinc, all to pass a 300-mesh sieve, together with some requirements as to grading according to size of particles. Close grading of size is more important than excessive fineness.

Spelter was formerly obtained from galvanizers' dross and other metallic zinky material by distilling in large bottle-shaped graphite retorts, commonly about 36 in. long and 20 in. in diameter. Furnaces with a battery of such retorts, commonly oil-fired, are still in use. Distillation of a charge requires about 18 hr. and a use of about 2 lb. of coal (or its equivalent of oil) per pound of dross and the labor of one man per shift per four retorts.

Some spelter is still produced in this way, but the quantity is greatly reduced and these furnaces are now used chiefly for the production of zinc dust, as being more profitable.

The treatment of galvanizers' dross and other zinc junk offers no very troublesome metallurgical problem, the zinc being simply boiled off and the vapor condensed either as spelter or as dust, the latter being accomplished by sudden chilling to a temperature of 320 to 415°C., which precipitates the zinc as snow, so to speak, instead of as rain. For this purpose a cast-iron canister may be used, and one 2 ft. in diameter by 4 ft. in height may collect 260 lb. of zinc dust in 24 hr. Either for spelter or for dust a commercial recovery of 80 per cent is about what is realized from galvanizers' dross. The loss is chiefly by retention in the residue of iron and lead that accumulates in the bottom of the retort until it is pulled out and broken up. There is a similar retention of zinc in connection with the cupriferous residue that accumulates in the distilling of zinc from old die-casting junk.

The zinc dust that is used by the electrolytic zinc producers is manufactured by atomizing molten spelter with a blast of air. There is a small production as a by-product from hot-dip galvanizing plants. In the modern technique of pipe galvanizing, and especially that of electrical-conduit galvanizing, the present practice is to blow through the pipes and tubes with dry steam under very high pressure. This gives a very fine dust, averaging upward of 95 per cent zinc as metal, that is collected by suitable means.

Zinc Burning or Zinc Fuming.—This is a process of reducing zinc oxide, which is distilled as vapor that is burned immediately. Theoretically, the metallurgical reactions are unchanged, but whereas in the recovery of zinc as spelter it is aimed to avoid oxidation of the vapor, the purpose is now to promote it, and to collect the oxide floating in the gas of combustion by filtering it through cotton bags. This introduces problems of cooling the products of combustion and dealing with them otherwise.

With ore free from lead and cadmium, and allowing coal ash, etc., to settle in the flue leading to the baghouse, oxide assaying 80 per cent zinc (the theoretical) and snow

white may be collected. The particles under a microscope will be in fractions of a micron ($\frac{1}{1000}$ mm. in diameter). The details of temperature, condensation, etc., that may cause these particles to be acicular, or of more equal dimensions or otherwise, will not be discussed here, nor the merit or demerit of different forms.

If the ore contains cadmium, it will go over into the fume, and will give it a color ranging from slightly yellow to distinctly brown. A slight yellowish tinge may be discharged, however, and it is possible to make a good grade of oxide from ore containing 0.3 to 0.4 per cent cadmium.

If the ore contains lead, it will surely be volatilized and filtered out with the fume as sulphate or some more complex oxidized form. The fume will no longer be capable of classification as "lead free," but will still be a valuable commercial product.

If the ore contains a good deal of lead, the product will be what is called a "leaded zinc," which is so valuable as a pigment that to some extent pig lead is melted and volatilized to boost a product derived directly from ore.

Zinc oxide of the highest grade is made by burning spelter; this is known as the French process and the product, French oxide. Zinc oxide as a finished commercial product is obtained directly from ore by means of the Wetherill furnace. Impure zinc oxide has been produced as a concentrate by the Pape process, by the Bartlett process, and by reducing in a reverberatory furnace, but those processes are now but little used, if at all. Recovery of zinc oxide from the blast furnace smelting brass junk is an important process practiced at Carteret and Perth Amboy, N.J., and Laurel Hill, L.I.

The present summary will treat only of the Wetherill process, the Waelz process, and slag fuming.

The fume collected from metallurgical by-products or waste products appears to run everywhere about 65 to 70 per cent zinc, the remainder being chiefly lead. This filtered fume is not an ideal product for re-treatment. It is fluffy, of low weight per cubic foot, and difficult to handle mechanically, either for shipment or for subsequent treatment. It may have to be densified by mechanical compression or by nodulizing by furnacing and may have to be delead.

Beneficiation of this fume may occur in the following ways, all of which exist in present American practice:

1. Return to the process of electrolytic extraction.
2. Delivery to manufacturers of lithopone (a hydrometallurgical process).
3. Delivery to manufacturers of lead-zinc pigment.
4. Delivery to zinc distillers. (With them it is not a warmly welcomed product unless it has been delead and nodulized. Without nodulizing it may, however, be mixed with roasted ore prior to sintering.)

Wetherill Process.—A distinguishing feature of the Wetherill furnace is the grate, which consists of a series of cast-iron plates, about 6 in. wide, 1 to 1.5 in. thick, and of length corresponding with the width of the furnace, which may be about 6 ft., these plates being perforated by conical holes about 0.25 to 0.4 in. in diameter on the upper side of the plate as it is to lie in the furnace and 1 in. in diameter on the lower side, there generally being about 100 holes per square foot. The purpose is to prevent a bed of ore and coal on the surface from sifting through very much and to prevent the holes from blinding. In some practice, the bars are perforated with narrow slots instead of conical holes. The bars rest on ledges in the side walls of the furnace. The ash pit is designed for operation of the furnace with an undergrate blast.

Furthermore, the two types of Wetherill furnace known as the Eastern and the Western differ only in details of design. The Eastern Wetherill is used at Palmerton, Pa. The Western Wetherill is used in the plants west of the Alleghenies. Exceptions to this generalization may be found in instances where furnaces of the Eastern

type have been built and operated more or less experimentally in Western plants. At Palmerton the ore that is treated is the franklinite concentrate from New Jersey. The Western plants treat ore from Tennessee, the Tri-State district, and from the region west of the Rocky Mountains.

The Eastern Wetherill consists of four or more hearths built together with a common back wall and with common side walls. The products of combustion from each hearth escape through an opening in its arch and are led to a chamber where the zinc vapor is completely oxidized, thence passing through a cooler to the baghouse.

The Western Wetherill comprises a series of hearths, separated only by low side walls and covered by an arch that is common to all the hearths comprising a block, the products of combustion being conveyed away from the end of the block.

In one plant where there were furnaces of both the Eastern and Western type, operated under identical conditions, no material difference in results was observed.

A Western Wetherill furnace of good design may have 10 hearths, each 6 × 12 ft., and may burn 24 to 25 tons of calcined ore per day mixed with 1.2 tons of coal, charging being done twice per day, and extraction of zinc from an ore of 70 per cent grade being about 87.5 per cent. Air pressure under the grate is equal to 2.5 to 4 in. of water. Length of furnace campaign may be 3 years.

Among plants, practice varies in operating details. The ore may be mixed with all the coal and so spread upon the hearth, or a bed of coal may first be laid and the mixture of ore and reduction coal then be spread on it. Three charges may be burned per 24 hr., or even four. The number of furnaces to a block may be 8, 10, or 12. The hearths may be as wide as 13 ft., *i.e.*, crosswise of the block. There are working doors on each side of the block, and the furnace personnel attends to one hearth after another. Mechanical charging has been satisfactorily applied, in which application all the coal is mixed with the ore.

With the Wetherill furnace it is necessary to counteract the tendency of the blast to break through the charge, making blowholes and craters. This requires constant attention. It prevented the mechanicalizing of the Wetherill furnace after the fashion of the traveling grate in steam-boiler practice, owing to the tendency of the air under pressure to break through along the sides and to slag and stick there. A great step in advance occurred when the New Jersey Zinc Co. began to make up the charge out of a briquetted mixture of ore and coal. The charge could then be burned like anthracite coal on a domestic grate, and the working doors of the furnace had no longer to be sealed. Obviously this opened the way to the mechanical Wetherill process.

In the operation of the mechanical Wetherill furnaces the charge of ore, plus about 20 per cent of coal, plus waste sulphite liquor from paper mills as binder, is compressed into hard briquettes, their shape being like that of a small pillow 2 in. square and about 1.5 in. through the thickest part. The grate bars of cast iron, which travel over sprockets at each end of the furnace, are 12 ft. long, which is the same as the width of the Western Wetherill furnace.

In operation the grate passes under a feed hopper from which it gets a bed of coal briquettes (of the same size as the ore briquettes), which are spread mechanically to a depth of 6 to 6.5 in. The coal briquettes pass through an ignition zone after which the grate receives from an overhead hopper a bed of ore briquettes about 6 in. thick. Reduction of zinc oxide and removal of the products of combustion then proceed according to the same principles as in the hand-operated furnace. Sticking of the charge to the side walls of the furnace is prevented by making them of water-cooled plates.

The mechanical Wetherill does away with the onerous labor conditions of the hand-operated furnaces, affords a much greater capacity per square foot of grate

Lead
with
Zn

surface, and by virtue of the intimacy of the mixture of briquetted ore and reduction coal gives an improved percentage of zinc extraction.

The Waelz Process.—This is a process of zinc reduction and burning by means of a revolving cylinder, internally heated to a high temperature, the mechanicalization being similar to the cylindrical furnace used for making cement. The Waelz furnace is built in sizes from 40 ft. in length and 6 ft. in diameter up to 160 ft. in length and 12 ft. in diameter. The slope downward from inlet to outlet is usually about 3 per cent. The rotation is generally about one turn in 55 sec., but it may be speeded to one in 30 sec. or retarded to one in 120 sec. For the largest furnace the power requirement is 25 to 30 hp., and the labor ranges from two to six men per shift. Ore and coke are mixed before charging. In the treatment of some low-grade calamine, the addition of coke has been as low as 10 per cent. In the treatment of retort residues, there may be sufficient unburned coke to allow the charge into the Waelz furnace to be self-burning.

In a plant in Upper Silesia, burning calamine with 12 to 15 per cent zinc, mixed with 25 per cent of reducing coal, 5 to 10 per cent of firing coal was used, and a zinc extraction of 95 per cent and a fume assaying about 66 per cent zinc and 6 per cent lead were obtained. About 160 tons of ore per furnace per 24 hr. was run. In the United States at the present time the Waelz furnace is used extensively in burning zinc out of current and old accumulations of distillation residues. A plant treating 300 tons of residues daily may yield 40 tons of fume or roughly 30 tons of zinc in fume. The yield is of course always commensurate with the quantity of zinc in the material that is treated.

It has been remarked before that even in good distilling in retorts about half the zinc in the residues is in oxidized form, perhaps partially as ferrate and silicate. Under the fierce internal heat of the Waelz furnace, further reduction is accomplished, and even a considerable proportion of zinc sulphide may be decomposed, reduced to zinc vapor, and burned. In this, as in other zinc-burning processes, the heat that is required endothermically for reduction is of course restored exothermically by combustion of the vapor.

If the Waelz fume is derived from leady ore, the fume itself will be leady. The fume derived from retort residues, however, will be low in lead inasmuch as such residues have been derived from ore previously delead. Such fume may therefore be returned to the ordinary process of distilling. This is done by mixing it with roasted ore prior to sintering.

Slag Fuming.—The treatment of slags from lead-smelting blast furnaces for extraction of their zinc content and recovery as oxidized fume is done on a large scale at East Helena, Mont., Tooele, Utah, Trail, B.C., and Kellogg, Idaho. The Bunker Hill plant at Kellogg, as the latest construction, sufficiently exemplifies the methods at the others.

Hot slag from the primary furnaces is transferred to the slag fumers. Some cold slag may be added. The slag-fuming furnace is 15 ft. long by 8 ft. wide and of standard water-jacket construction. On each side there are 14 double-inlet tuyères, each side being fed with a Babcock & Wilcox pulverizer of 4080 lb. of coal per hour rated capacity. They are designed to feed coal against internal pressure up to 10 lb. per sq. in. The pulverized coal (upward of 80 per cent through 200 mesh) is delivered to the tuyères in a primary air stream comprising about 48 per cent of the total air flow. The remaining 52 per cent enters the tuyères as secondary air. Two Ingersoll-Rand turboblowers, maximum rating 6910 cu. ft. each at 8 lb. gauge, supply the furnace air.

The coal-air mixture forced through the slag both supplies heat and effects the reduction of zinc oxide. The slag is treated in batches, each batch comprising a

furnace cycle, divided into three periods, viz., charging, reducing, and tapping. Coal and air are delivered to the tuyères continuously throughout the operation, and the reduction period is about 65 per cent of the time of the cycle.

The dust-laden gas leaves the furnace at somewhat over 1100°C., enters the waste-heat boilers at 925 to 1040°C., and finally enters the baghouse at 200°F. The slag is dezinked down to about 1 per cent Zn. The fume assays 63 per cent zinc and 10 per cent lead and weighs approximately 40 lb. per cu. ft. It is densified and delead by mixing with about 1.5 per cent by weight of minus- $\frac{1}{4}$ -in. crushed coke and is calcined by passing it through a revolving cylinder, 75 ft. long by 7 ft. diameter, fired by either oil or coal dust, the temperature being about 500°C., at the feed end and about 1260°C. at the discharge end. Passage through this kiln nodulizes the raw fume, increases its weight to about 185 lb. per cu. ft., raises the zinc content to about 72 per cent, and reduces the lead to about 1.5 per cent. Fume from this kiln is delivered to a baghouse, whence a product with about 50 per cent lead and 23 per cent zinc is returned to the lead-smelting system via the Dwight-Lloyd sinterers.

The Bunker Hill plant was designed in 1943 for the treatment of 300 to 400 tons of hot slag per day. The operating personnel comprises 14 men per 8-hr. shift.

The production of zinc from the slags of lead smelting has now become an important process in the United States and in Canada. It gets the zinc from what are classed as lead ores and thus increases the extraction from an original zinc-lead sulphide ore by a substantial quantity. Moreover, it brings accumulations of old slag into the classification of new zinc deposits. In 1944, the three major plants in the United States treated about 510,000 tons of slag, which yielded 78,500 tons of oxide fume, containing about 55,000 tons of zinc. The cost per ton of slag is relatively low, but obviously it is substantially more for cold slag than for molten, and of course it is increased if nodulizing and deleading has to be done.

Continuous Distilling.—Obstacles in the way of designing a furnace for continuous reduction and distilling of zinc have been (1) difficulty of integrating in one operation the two stages of intermittent distilling, viz. (a) preliminary reductions and (b) the reduction of zinc oxide itself; (2) trouble from the ore becoming sticky and so hanging in a vertical shaft through which it was expected to descend; (3) inability of zinc vapor to find egress through a long column of fine ore, which cannot be "spiesed" as in the ordinary horizontal retort. Following many failures to accomplish continuous distilling, four processes have come into commercial use, although not all of them are in use at the present time. These are summarized in the following sections.

Trollhattan Process.—Some intelligent work was done in experimental plants to subject calcined ore to prereluction and then transfer it to an electric furnace heated by the resistance of a bath of molten slag into which dipped the graphite electrodes carrying the current. Although with such a furnace lead could be tapped from the bottom and spelter could be condensed from zinc vapor escaping from the top, the loss of zinc in the slag was prohibitive apart from other objections.

At Trollhattan, in Sweden, loss of zinc by scorification was minimized by making a high-temperature bisilicate slag, e.g., 50 per cent SiO_2 , but in the absence of prereluction the zinc vapor was condensed mainly as blue powder. The blue powder was melted to spelter by the ingenious Cornelius process in which by putting it in a suitably heated, revolving cylinder, oxide coatings of the zinc globules were rubbed off, thus allowing the globules to coalesce. The crude spelter thus obtained was refined by redistilling in another electric furnace. By this process many thousands of tons of spelter were produced.

Roitzheim-Remy Furnace.—In this furnace a battery of 22 annular retorts about 24 in. in diameter and about 6 ft. in height are arranged in pairs within a common combustion chamber. Inside of each retort is a vertical tube with apertures in its

cke
de-lea

walls. The material to be distilled is charged into the annular space around the central tube, the apertures of which allow the gas and vapor to escape from the retort into the tube. The two tubes of a row are connected across and thence communicate with the condenser sticking out from the wall of the furnace, which is luted in as usual. It is uninteresting to go further in description of the complicated construction of this furnace and the details of its operation.

A plant in Berlin equipped with a considerable number of these furnaces operated continuously with charges of galvanizers' ashes, which is a material not requiring pre-reduction and not becoming gummy when heated. Each retort received a charge of about 1000 lb. and yielded in a single tap per 24 hr. about 440 lb. of spelter plus about 80 lb. of zinc dust as ladle skimmings and prolong dust. These results were considered satisfactory.

Some trials of the Roitzheim-Remy furnace in ore distilling in other plants were unsatisfactory.

New Jersey Zinc Co.'s Process.—Success in using briquetted ore on the Wetherill grates contributed to this process of continuous distilling, in which the charge of ore and reducing coal is briquetted in the same way. Prior to charging into the retort, however, the briquettes are coked by passing them continuously through a vertical chamber of horizontal cross section in which they are coked by means of the exhausting gases from the combustion chamber of the distilling furnace, these gases entering the coking chamber at 750 to 900°C.

The distilling furnace as a unit comprises either 8 or 16 retorts. The retorts are rectangular in horizontal cross section, commonly 6 ft. × 12 in., but retorts of 7 ft. × 12 in. are in successful use. The long sides of the retort are laid up with shapes of silicon carbide carefully fitted so as to be gastight. The height of the retort that is heated is ordinarily 25 ft., but there are extensions at top and bottom for the mechanism of introducing fresh briquettes and discharging those that have been exhausted at the bottom. The retorts are operated continuously, but the charge is introduced in batches at proper intervals.

The condenser consists of two parts, the first being an inclined conduit directly connected with the retort, in which the gases are cooled rapidly, and a second part comprising a sump in which the molten spelter is collected and in which the cooling of the zinc vapor is completed at a relatively slow rate in order to avoid precipitation as blue powder by excessively rapid chilling. The condenser has baffles to zigzag the flow of vapor through it.

The exhaust gases from the condenser are scrubbed to eliminate any remains of zinc vapor and are then returned as nearly pure carbon monoxide to the combustion chamber of the furnace, thus affording 20 per cent of the heat required to fire the retort. A temperature of 1300°C. in the combustion chamber, a zinc elimination of 96 per cent, and a recovery of 92 per cent of the content of the charge may be realized. With a furnace of 16 retorts treating calcined sulphide ore of the ordinary grade of flotation concentrates, a yield of 60 tons of spelter per day may be realized. The retort life is 3 to 5 years.

The production of blue powder in the New Jersey process is very small, being only that which is scrubbed out of the gas escaping from the condenser. The coking of the charge effects preliminary reductions and reduces the production of carbon dioxide within the retort. The reduction of carbon dioxide is substantially completed in the upper extension of the retort by passing through the hot coked briquettes which likewise filter out particles of charge entrained by the gases. Any blue powder formed on the descending charge is thus automatically returned to the reduction zone of the retort. All this was a perfection of the old idea of passing the gas and vapor from the zinc retort through a filter of incandescent coke, as in the Kleeman condenser of former times.

The New Jersey continuous process has had the advantages of giving an increased extraction of zinc, less production of between products, less requirement for coal for fuel (this saving being enhanced by utilization of the carbon monoxide gas from the condensers), a saving of labor, the production of an improved grade of spelter, and the general advantages resulting from steady conditions that are capable of close regulation. On the other hand it is subject to increased cost for labor and material in briquetting the charge, and the amortization of a costly plant.

New Jersey vertical retorts are in use at Palmerton, Pa., Depue, Ill., Meadowbrook, W. Va., Avonmouth, England, and Oker, Germany. Having been first commercialized in 1929 and having been in steady use since then, this process is now thoroughly established.

The St. Joseph Lead Co.'s Process.—This process, which is the most successful of any of the proposals for electrothermic distillation, was developed from the patented ideas of E. C. Gaskill. Instead of trying to combine zinc smelting and lead smelting, as in the fusion processes of prior inventors, he conformed to the simple principle of zinc reduction and distillation with internal heating instead of external. The process as originally introduced at Josephstown, Pa., in late 1930 contemplated only the production of zinc oxide.

Calcined ore is sintered under conditions to produce an unusually hard sinter. By-product coke is used for reduction fuel. Both ore and coke are sized, then mixed in equal-volume proportions, and preheated in a revolving kiln to a temperature of about 850°C.

The preheated mixture is charged into columnar furnaces, 69 or 96 in. in diameter inside and 37 to 40 ft. over-all in height. Near the top of this shaft four or six electrodes protrude into it, and a corresponding set enters near the bottom, the height between each group of electrodes being 26 ft. Inasmuch as the charge is to be the resistor, the carbon must be constantly maintained in excess of what is required for reduction of zinc oxide. Each furnace contains upward of 25 tons of charge, and about 18 hr. is required for passage through the furnace. Internal temperature is about 1200°C. Gas and vapor escape through 12 openings, disposed in groups of three on each of four levels within the electrode boundaries, and the vapor is burned to oxide which is baghoused in the usual way.

The original Josephstown furnaces were designed only for the production of zinc oxide. Because of the relatively enormous output of zinc vapor per furnace day, it was quickly found that surface condensers of the area required would be very large. Hence, attention was turned toward developing a more compact condensing means. That problem was solved by the development of a special condenser which is described in U.S. patent 2070101, Feb. 9, 1937, issued to George F. Weaton and H. K. Najarian. This condenser is in effect a U tube containing molten spelter, just as a manometer contains mercury, but one limb is of circular cross section, connecting with the furnace and being capable of temperature control. The vertical limb leads to a gas washer and of special design which is described in U.S. patent 2298139, Oct. 6, 1942, issued to Carleton C. Long and George E. Deeley. A pipe with a vacuum-control valve connects the gas-deduster discharge to a mechanical exhauster. The idea is that the gas and vapor shall be drawn through the molten spelter contained in the condenser, and that following condensation of the zinc, the gas shall be drawn through the washer. The gas bubbles through the molten zinc. Periodically, zinc is tapped from a "tapping well" which communicates with the lower part of the condenser.

The molten zinc is preferably kept at a temperature of 500 to 550°C. The vapor enters the condenser at a temperature of about 850°C. In the vapor-collecting ring surrounding the furnace there is a considerable drop of vapor temperature, but not enough to condense any appreciable amount of metal, as the dew-point temperature

is ordinarily about 830°C. The power required for operating the vacuum pump and CO compressors when condensing 100 tons of spelter per day is approximately 475 hp. Spelter assaying 99.97 per cent zinc is produced. Zinc dust recovered from the washer depends on the vapor pressure of the condenser exit gas and is about 3 to 10 per cent of the condenser production of spelter.

Spelter production is about 18 tons per furnace-day for the 69-in. D furnaces. Operating labor in the furnace plant is approximately 5.5 man-hours per ton of spelter produced. Over-all recovery in spelter and other salable products is 90 to 93 per cent. Of the loss, about 4 to 5 per cent occurs through zinc in the finally discarded residue. Total smelter power requirements are 3258 kw.-hr. per ton of zinc equivalent produced. This is for 54 to 55 per cent Zn concentrates. For higher tenor feed, recovery is somewhat higher and power requirement somewhat lower. Furnace power is 78 to 79 per cent of what is required for the entire plant operation.

It appears from these data that the use of electrothermic power at Josephstown is much less than what it was at Trollhattan, when electrothermic distilling was being performed there. One reason for the difference was that at Trollhattan the gangue of the ore was fused and run off as a slag, which was a great consumer of energy, whereas at Josephstown the gangue is discharged unfused.

Spelter Directly from Slag.—The St. Joseph Lead Co. since 1941 has been developing a method for the recovery of zinc as spelter directly from slags of lead smelting at Herculaneum, Mo., containing 12 to 16 per cent zinc. In 1944, several hundred tons of spelter were produced there by this method, and it is believed that large-scale production is imminent.

The reduction of zinc is accomplished in an electric furnace in the form of a horizontal cylinder of 1-inch steel plate, 42 ft. long by 15 ft. 4½ in. in diameter, outside dimensions, which are reduced to about 37 × 11 ft., inside, by refractory linings. Slag is fed through a small water-cooled hole in one end wall, about 12 in. above the maximum slag level, and spent slag is withdrawn through a water-cooled tap in the opposite end wall, matte and iron being tapped through a lower hole. Electric power is introduced by six carbon electrodes, 30 in. in diameter, spaced on 5-ft. 6-in. centers in line along the top of the furnace. Gas and vapor are led to a Weaton-Najarjian condenser, 31 ft. long, with associated Long-Deely gas dedusters. Metal tapped from the condensers is drawn to a large settling furnace, whence spelter of Prime Western grade, containing about 1 per cent lead, is obtained.

Coke breeze, for reducing carbon, thoroughly dried, is distributed by a Deeley coke slinger over the top of the slag bath throughout its length. The depth of the slag bath, into which the carbon electrodes dip, is 10 to 30 in., the depth being measured by a bar let down through a hole in the roof of the furnace. The slag bath is the resistor. The electrodes that dip into it are raised and lowered by motor-driven staffs. The operation proceeds essentially on a continuous basis, but the feed and discharge of the slag are semicontinuous. The exit slag is about 80 per cent of the weight of the incoming slag when the latter contains 12 to 13 per cent zinc.

It is expected that in commercial operations the power consumption will be 800 kw.-hr. per ton of slag of 14 per cent zinc; the coke consumption, not over 7.5 per cent of slag weight; the electrode consumption, not over 10.5 lb. per ton of slag; stripped slag to contain not over 20 per cent of the zinc charged; and the over-all recovery as slab zinc, 75 per cent of the zinc in the feed.

Spelter Directly from Brass Scrap.—Heretofore the only method of recovering zinc from brass scrap has been to vaporize it, let it burn, and collect the oxide fume by filtration (baghouse). In the Wilkins-Poland process, recently developed, the scrap is melted and is fed into a sealed distilling furnace, which is lined internally with carbon blocks. The temperature of the furnace is raised by electric current passing

through graphite resistors. Zinc is distilled off, condensed, and cast directly into slabs. The condensers operate simply and effectively, there being no diluting gas in the zinc vapor entering into them. In starting the operation, an atmosphere of nitrogen is established in the melting furnace and the distilling furnace is flushed out with nitrogen until it becomes filled with undiluted zinc vapor. After the zinc is distilled off, the residual copper is drawn off and fire-refined in the ordinary manner. Mr. R. A. Wilkins informs me that as a matter of operating economy, it is not possible to reduce zinc to much below 2 per cent, that quantity being discharged in the copper going to the fire-refining operation. From brass scrap averaging 30 per cent zinc or more the recovery of zinc in the form of slabs is upward of 90 per cent.

CADMIUM

By W. R. INGALLS¹

Cadmium a By-product.—Metallurgical literature has no record of any ore beneficiated for cadmium alone, and the cadmium of commerce is derived from zinc ore, with which cadmium is generally associated. Zinc ores free from cadmium, e.g., the ores of the Franklin and Stirling mines, New Jersey, and of Broken Hill in Rhodesia, are rare.

Blende concentrates of 50 to 60 per cent grade have contained (in production of important tonnage) as much as 1 per cent Cd, which is unusually high. The concentrates from the Tri-State district average 0.3 to 0.4 per cent Cd, which is high. The concentrates from mines west of the Rocky Mountains seldom are higher than 0.2 per cent.

In the periodic system of the elements, cadmium is in the same group with zinc. Its properties and compounds are similar. Its metallurgy is also similar. Cadmium has a melting point of 320°C. and a boiling point of 778°C., while the melting point of zinc is 415°C. and the boiling point 905°C. These conditions, together with the lower reduction temperature of cadmium oxide, indicate a means for separating cadmium from zinc.

Cadmium in spelter is viewed, if not as an impurity, at least as an alloying element that may be objectionable, its special effect being hardening. However, for some purposes, a little cadmium in spelter is desired, and 0.4 per cent may be permissible, even in spelter for rolling. Cadmium in spelter for brass making is completely volatilized at the temperature of that process, and in bygone days an immense quantity of cadmium must have been lost in the fumes from these furnaces. The arrangement of brass mill furnaces is such that the collection of fumes is economically impracticable. At the present time, however, the brass makers are mostly using high-grade spelter (cadmium-free).

The salts of cadmium are poisonous, materially more so than are the corresponding salts of zinc. A dose of 0.03 g. of a cadmium salt is fatal to animals, and very small quantities are poisonous to human beings. Cadmium may be easily electroplated, and when so applied adheres firmly and resists bending without cracking, but it is readily attacked by acetic and tartaric acids, appreciably more so than zinc. In view of its ease of solubility and its toxicity, the use of cadmium for articles that may come into contact with foodstuffs is inadvisable.

Pyrometallurgy—Early.—Cadmium compounds, sulphide and oxide, being more volatile than the corresponding compounds of zinc, loss of cadmium begins to occur from the first furnace operation. In normal roasting, even with Tri-State ore, this loss may not be very high. Raw ore, assaying 0.4 per cent Cd, may be expected to give a roasted product of the same assay, which would imply a cadmium loss of about

¹ A condensed version of this article appears in *Trans. A. I. M. E.*, Vol. 159, 1944.

15 per cent. Roasted ore, assaying 0.4 per cent Cd when distilled at ordinary furnace temperature yielded spelter containing about half of what was in the ore charged.

The first draw of spelter under these conditions may assay 0.8 per cent Cd (accounting for 22 per cent of the cadmium recovery), and after the several draws of spelter have been equalized the cadmium content may average 0.35 per cent. If therefore 2000 lb. of blende averaging 0.35 to 0.4 per cent Cd is roasted and distilled, there may be obtained 1000 lb. of spelter, assaying 0.35 per cent Cd or 3.5 lb. content, which entering into Prime Western spelter will be sold at the spelter price.

It will be observed from the previous outline (summarizing conditions prior to the introduction of sintering) that the main loss of cadmium occurred in the distillation process and by failure to condense, which could be ameliorated by attaching a prolong to the condenser, thus collecting additional zinc dust, relatively rich in cadmium. This was the basis of cadmium metallurgy, especially practiced in Upper Silesia, prior to the introduction of the process of electrolytic zinc extraction. The primary zinc dust containing 5 or 6 per cent Cd, mixed with some charcoal, is distilled and redistilled until finally, by thus fractionating, a metal containing 99.5 per cent Cd is obtained. The low temperature of this distilling permits the use of cast-iron retorts and sheet-iron condensers, which either are lined with some refractory material or are whitewashed with lime inside so as to prevent contamination by iron.

Electrometallurgy.—With the introduction of the process of electrolytic zinc extraction in the United States and Canada in 1915–1916, that process became a large source of cadmium production, inasmuch as both cadmium and copper were bound to be leached along with zinc and necessarily had to be precipitated prior to zinc electrolysis. This purification is effected by adding zinc dust to the solution in such proportion as to throw down copper, which is filtered out and sent to copper smelting. Such a precipitate may assay 70 to 75 per cent Cu, 1 per cent Cd, and 3 per cent Zn (reflecting the excess of zinc necessarily used). To the filtrate a large excess of zinc dust is then added, and the purified liquor is filtered off, leaving a zinc-cadmium sludge.

The zinc-cadmium sludge may be stockpiled in heaps, promoting oxidation and solubility in acid; or oxidation may be expedited otherwise, *e.g.*, by spreading it on a platform and steaming it. Either way the cakes will probably have to be disintegrated, which may be accomplished by attrition in a pebble mill. There may have to be a precipitation of cobalt, requiring the use of some reagent, *e.g.*, nitroso-beta-naphthol or potassium xanthate. However, the electrolysis of cadmium sulphate solution is not very sensitive to impurities, and their removal by zinc-dust precipitation is generally adequate. It is impossible to wash all the entrained zinc from the cadmium sludge, so zinc is a cumulative impurity in the electrolytic cycle. It is controlled by precipitation with milk of lime. It is only necessary to maintain the zinc in the electrolyte at a point where the excess of cadmium over zinc in the spent electrolyte is of the order of 10 to 15 g. per l.

In the final stage of cadmium recovery, the sludge is dissolved in spent electrolyte and subjected to electrolysis either with rotating cathodes or with stationary cathodes, which are of aluminum as in zinc electrolysis. Cadmium has a strong tendency to deposit as buds, sprouts, and trees. These are obviated by the use of rotating cathodes, or with stationary cathodes when cell temperature is maintained at 30 to 35°C. and with the addition of glue to the electrolyte. A deposition of 1 lb. of cadmium per 1.04 kw.-hr. of direct current, compared with 1.5 kw.-hr. for zinc, is realized. The plant factor is of course higher by virtue of the loss in changing from alternating current to direct current and the mechanical power that is required in plant operation.

In American practice, stationary cathodes are generally used and with the same cell construction and operating conditions as for the electrolysis of zinc. With

3.5-in. spacing between cathodes, the cell voltage is approximately 2.6 to 2.7 and the current density about 4 amp. per sq. ft., but in some practice it is as high as 10 amp. The cell feed may contain per liter 100 g. of cadmium, 80 of zinc, and 70 to 80 of H_2SO_4 , and may be as high as 200 g. of cadmium and as low as 30 g. of zinc. Cathodes are stripped every 12 hr. in some practice, every 24 hr. in other practice. They are melted in a cast-iron pot, electrically heated to 400 to 450°C., under a thin layer of caustic soda to prevent oxidation; and the pot is well hooded to carry off oxide fume.

After the cadmium has been dissolved and is ready for electrolysis, the recovery as ingot is about 96 per cent. If the raw ore is roasted without special means for collection of dust and fume, the over-all recovery may be 84 to 85 per cent. If the roasting furnaces are connected for sulphuric acid manufacture with thorough provisions for collection of dust and fume, over-all recovery may be 90 to 95 per cent. Electrolytic cadmium is of 99.95 per cent grade, or better.

Hydrometallurgy.—In the use of roasted Tri-State ore for the manufacture of ordinary zinc lithopone, it is necessary to remove cadmium just as it is for electrolysis. Such ore has been partially decadmiumized by a water leach, but that has not been a general practice, which is rather to take out the cadmium with an acid leach. From such a solution the cadmium is precipitated by addition of an excess of zinc dust, affording a zinc-cadmium sludge. As to purification the requirements for a solution of zinc sulphate for lithopone are almost as refined as for electrolysis. The sludge obtained in this way may assay 35 per cent Cd, 46 per cent Zn, and 21 per cent water; or 54 per cent Cd, 16 per cent Zn, and 30 per cent water. These analyses vary naturally according to the excess of zinc dust that is used. The cadmium in such sludge is sold by the manufacturers of lithopone at something like 75 to 80 per cent of the price for cadmium in sticks, pencils, and other refined forms, manufacturers of cadmium pigments being the buyers. Digesting the sludge with sulphuric acid and obtaining a solution of $CdSO_4$ or $CdSO_4 + ZnSO_4$, the sulphides of those metals may be precipitated with a solution of barium sulphide to make cadmium lithopone; or a precipitate of cadmium sulphide may be thrown down from an acid solution by H_2S .

Pyrometallurgy—Recent.—When the sintering process for desulphurizing and fritting zinc ores was introduced, it was immediately noticed that the smoke issuing from the chimney dispersing the gases frequently showed the brown coloration of cadmium oxide and, concurrently, that the cadmium content of the sintered ore was reduced or even all but entirely eliminated. It was observed moreover that following the introduction of roasters of the McDougall type, roasting flotation concentrates with cyclones, improved dust-settling chambers, Cottrell precipitators, etc., as appendages, there was obtained dust and fume relatively rich in cadmium, *e.g.*, as high as 4 per cent Cd and all of it water-soluble.

An experience with an ore containing 1.05 per cent cadmium, or 21 lb. per ton, following introduction of sintering, is illuminating. From a roaster (of the McDougall type) 80 lb. of heavy dust assaying 4 per cent cadmium was collected from 2000 lb. of raw ore. There was a further settlement of fume, but 1 lb. of cadmium per ton of ore passed through the Glover towers and into the sulphuric acid. The calcines weighed 1700 lb. and assayed 0.65 per cent cadmium, and the sintered cake assayed 0.375 per cent cadmium. The first draw of spelter weighed 204 lb. and assayed 1.25 per cent cadmium; the subsequent draws, aggregating 680 lb., assayed 0.08 per cent cadmium. The cadmium accounting in terms of pounds per ton of raw ore was as in the table on page 472.

It is clear that nearly all the cadmium in this ore could be recovered by providing suitable means, especially for expelling all the cadmium from the calcines (leaving none to go into the retorts) and collecting all the dust and fume from both the roasters and the sinterers. In the experience here summarized the volume of gas from the

sinterer was 462,000 cu. ft. at 218°F. per ton of calcined ore, which could have been greatly reduced by sealing the side openings between pallets and wind box (see the chapter on Pyrometallurgy of Zinc).

In flue dust from roasters.....	3.2
In fume from roasters.....	5.8
In sulphuric acid.....	1.0
Loss in sintering.....	4.6
Content of first draw of spelter.....	2.6
Content of subsequent draws.....	0.5
Content of blue powder.....	0.5
Content of retort residue.....	0.2
Escape from condensers, by difference.....	2.6
Total.....	21.0

These observations became the basis of the improved metallurgy among zinc distillers, who in view of the increased demand for cadmium after 1935 aimed to recover the large cadmium content of Tri-State ore that previously had been wasted. In order to accomplish this, the process of sintering was adjusted so as to increase the elimination of cadmium, especially by preventing its condensation in the lower part of the bed on the pallets after it had been volatilized from the upper part, this being largely a matter of temperature control and technique. It was found also that by the addition of sodium chloride, anywhere from 0.5 up to 2.5 per cent, the well-known chloridizing reaction could be realized, with nearly complete elimination of both cadmium and lead. Another expedient was moistening the ore with a solution of zinc chloride.

These proposals were founded on the idea of decadmiumizing and deleading zinc ore with the objective of producing high-grade spelter. At this time, about 1930-1933, cadmium was in poor demand. Later it became worth while for zinc smelters to save cadmium that they had previously been wasting. This involved naturally a reduction of the volume of the sintering gases by better sealing of the wind box and precipitation of their fume by means of Cottrells.

In works practice the dust and fume from the roasters in oxidized form and the dust and fume from the sinterers, containing cadmium chloride, lead chloride, and any of the excess of zinc chloride that has been volatilized, are mixed and digested with sulphuric acid. Lead sulphate is filtered off. Cadmium may then be precipitated by the addition of zinc dust, and the filtrate containing zinc sulphate and zinc chloride is returned to the sintering process, while the cadmium precipitate is refined by distilling, or otherwise.

By the New Jersey process of refining spelter by redistillation, cadmium comes off in the form of cadmium-zinc metal or a cadmium dust, which is readily converted to metallic cadmium by any one of the several known methods. This was done prior to the war at Duisburg, in Germany, by the Thede and New Jersey processes in combination.

In addition to the methods already described, there is a good deal of cadmium produced by the silver-lead smelters, which in treating zinc ore obtain considerable quantities of cadmium in their flue dust. Treatment thereof for cadmium recovery has been sufficiently suggested without going into details.

Out of the production of metallic cadmium in the United States in 1941, aggregating 3220 tons, the electrolytic producers in Idaho and Montana afforded 970. There is also a considerable production of cadmium that is obtained as direct chemical compounds, especially cadmium sulphide, for which there is use as a pigment, either as such alone or in cadmium lithopone.

CHAPTER XVI

MERCURY

BY GORDON I. GOULD¹

History and Mines.²—Quicksilver, or mercury, seems first to have been mentioned by Aristotle, who referred to it as fluid silver (*argyros chytos*). Theophrastus, about 315 B.C., states that quicksilver is obtained from cinnabar rubbed with vinegar in a brass mortar with a brass pestle. Dioscorides, about A.D. 50, appears to have first mentioned the recovery of quicksilver (which he called *hydrargyros*, liquid silver) by distillation, stating, "An iron bowl containing cinnabar is put into an earthen vessel and covered over with a cup-shaped lid smeared with clay. Then it is set on a fire of coals, and the soot which sticks to the cover when wiped off and cooled is quicksilver." Pliny, about A.D. 50, reports both these methods. Agricola in his "De re metallica"[1], published in 1554, gives the first detailed description of several methods in use at that time, all distillation processes.

Although recorded production data are comparatively modern, Becker[2] estimates production in terms of 75-lb. flasks up to A.D. 1700, and thereafter with greater accuracy up to 1886. Since that time, fairly accurate records are available. Up to 1700, he estimates the world production as approximately 1,800,000 flasks; between 1700 and 1800 an additional 2,375,000 flasks were produced; from 1800 to 1900 Becker's estimate plus more accurate records indicate approximately 5,890,000 flasks; from 1900 through 1940, it is estimated that an additional 4,560,948 flasks were produced. The estimated total world production, therefore, approximates 14,625,000 flasks; although other authorities have reported it to be as high as 18,000,000 flasks.

It is interesting to note that the Almaden Mine in Spain has probably been responsible for more than one-third of the total production and the Idria Mine in Italy approximately one-quarter of the total production. Other large producers include the Santa Barbara mine in Peru, the Abbadia San Salvatore mine in Italy, the New Almaden mine and the New Idria mine in California, and the mines of the Chinese province of Kwei-Chau. Although quicksilver production in recent years has come from no less than 20 countries, Spain and Italy continue as the largest producers (approximately 70 to 80 per cent combined), with the United States third and Mexico and Canada following.

Within the United States many new mines have been discovered during the past few years under the impetus of increased prices and wartime demand; however, by far the larger part of production continues to come from the older mines and probably will continue to do so. This situation also exists throughout most of the rest of the world, although important recent discoveries have been made in Canada.

Production and Prices.—Table 1 indicates the widely fluctuating production and price range that is characteristic of the industry, even before the years cited.

This wide range of price has played an important part in governing the size of the quicksilver industry within the United States, where the ores treated are of much lower grade than in other countries. Only 10 mines contributed to the total American

¹ Consulting engineer, San Francisco, Calif.

² References in brackets are to similarly numbered references in the Bibliography at the close of the chapter.

production in 1922, whereas there were 197 producers in 1941. Likewise, the development of ore reserves, metallurgical progress, and long-range planning have been handicapped by the wide fluctuation in price and by market manipulation by foreign producers controlling the bulk of production.

TABLE 1.—PRODUCTION AND PRICES OF DOMESTIC QUICKSILVER, 1910-1944

Year	Production ^a	Price ^a	Year	Production ^a	Price ^a	Year	Production	Price
1910	20,330	47.69	1922	6,291	59.74	1934	15,445	73.87
1911	20,976	47.16	1923	7,833	67.39	1935	17,518	71.99
1912	24,734	43.03	1924	9,952	70.69	1936	16,569	79.92
1913	19,947	40.07	1925	9,053	84.24	1937	16,508	90.18
1914	16,330	48.95	1926	7,541	93.13	1938	17,991	75.47
1915	20,756	88.17	1927	11,128	118.16	1939	18,633	103.94
1916	29,538	127.16	1928	17,870	123.51	1940	37,777	176.87
1917	35,683	107.72	1929	23,682	122.15	1941	44,921	185.02
1918	32,450	125.12	1930	21,553	115.01	1942	50,846	196.35
1919	21,133	93.38	1931	24,947	87.35	1943	51,929	195.21
1920	13,216	82.20	1932	12,622	57.93	1944	22,100 ^b	126.17
1921	6,256	46.07	1933	9,669	59.23			

^a Production and price figures for the years 1910-1926 calculated to the 76-lb. per flask basis from the 75-lb. flask then used.

^b Estimated production, first six months 1944.

All prices are based on the average monthly quotation of *Engineering and Mining Journal*, New York.

Properties and Uses.—Quicksilver is the only metal that is liquid at all ordinary temperatures. (Gallium melts at 30.1°C.) This fact quite naturally was responsible for many early conjectures as to its true nature and, as well, gave it a rather mystic position in the hands of the early alchemists. Today, the same property makes it useful, if not indispensable, in many applications in industry, the sciences, and everyday use.

Quicksilver, the metal, has an atomic weight of 200.61, a valence of either 1 or 2, and a specific gravity of 13.595 at 4°C. The melting point is -38.85°C., below which it is a white malleable ductile metal. The boiling point is 357.25°C., above which it is a colorless vapor having a density of 6.7 to 7.03. As a metal, it has relatively low thermal and electrical conductivity and is soluble in nitric acid, aqua regia, and hot concentrated sulphuric acid, but is not soluble in hydrochloric or dilute sulphuric acid.

In chemical combination, it has a wide variety of uses. Although most of the salts are consumed in relatively small quantities, the bichloride (corrosive sublimate) and the chloride (calomel) are used in substantial quantity. Accurate information as to the specific uses to which quicksilver is put is neither compiled regularly nor is it probably very accurate; however, Table 2 shows in a general way the distribution and trend of the various uses. All figures are submitted by the authors as estimates, and it must be pointed out that the first two and the last two years cited represent wartime distribution. Especially in 1942 and 1943, this undoubtedly accounts for the large undistributed quantity listed under Other.

It is stated that half or more of the quantity shown under Redistilled for 1942 and 1943 was used in industrial and control instruments. In 1928, the dental preparations included at least some of what would otherwise be classed as redistilled.

TABLE 2.—ESTIMATED DISTRIBUTION OF USES OF QUICKSILVER

	1917 ^a	1918 ^b	1928 ^c	1942 ^d	1943 ^{d,e}	% ^f
Pharmaceuticals.....			5,493	8,088	14,192	28.37
Dental preparations.....			362	1,198	533	1.07
Chemical preparations.....			7,486			
Seed disinfectants.....			365	1,533	1,340	2.67
Drugs and chemicals, total.....	8,500	12,180	13,706	10,819	16,065	32.11
Fulminate.....	4,850	12,218	6,587			
Vermilion.....	3,130	1,900	2,450			
Felt manufacture.....	1,700	1,800	1,720	20		
Amalgamation.....	850	800	453	180	22	0.05
Antifouling paints.....	3,000	2,905		1,220	2,578	5.15
Electrical apparatus.....	2,700	2,687	2,556	4,550	2,988	5.97
Industrial and control apparatus.....	630	676	2,996	3,529	3,365	6.73
Catalyst (in electrolytic preparation of caustic soda and chlorine or glacial acetic acid).....			1,000	3,802	4,679	9.35
Redistilled.....				6,175	4,925	9.84
General laboratory use.....			628	294	331	0.66
Other, or not above classified or combined.....	1,000	1,000	2,846	17,148	15,077	30.14
Total.....	26,360	36,166	34,942	47,737	50,080	100.00

^a RANSOME, Quick silver *U.S. Geol. Survey*, "Mineral Resources of the United States," part I, 1917, p. 384.

^b RANSOME, Political and Commercial Control of Mineral Resources of the World, U.S. Dept. of the Interior, No. 4.

^c SCHUETTE, Quicksilver, *U.S. Bur. Mines Bull.* 335, p. 147.

^d Mineral Market Reports, Mercury in 1943, *U.S. Bur. Mines*, No. MMS 1141, p. 3.

^e Includes only January-November, 1943.

^f Percentage of total consumption, January-November, 1943.

The use of quicksilver in the felt-manufacturing industry has been largely displaced, owing to the health hazard and state prohibition of the further use of the skin-irritating mercuric nitrate; amalgamation has further and further been replaced by other precious-metal beneficiation processes (and the current wartime restriction order prohibiting the operation of gold mines); the fulminate consumption has been largely reduced owing to satisfactory substitution in military requirements; and antifouling paints continue at about the same pace, though resisting substitutes have been devised.

Electrical apparatus has probably shown a greater increase than is apparent in the figure for 1943, and industrial and control apparatus is increasing greatly; general agricultural uses and requirements by the textile industry may well advance in the near future in consumption of the organic mercurials.

Although there are many uses and many industries in which quicksilver has been substituted for or otherwise displaced, there have been a far greater number of new uses developed, the aggregate consumption of which indicates a gradually increasing demand for the metal which undoubtedly assures the requirement for increased production. This increased production will have to come from lower grade ores, and metallurgical efficiencies will necessarily have to be kept at the highest possible point.

Metallurgy of Quicksilver.—Although the metallurgy of quicksilver is probably one of the simplest, it has undoubtedly been subjected to as many variations as that

of the more refractory metals. The treatment processes are first limited in that there is only one important ore mineral. This mineral is cinnabar which is the sulphide (HgS), a bright vermilion mineral. Although varying from a bright vermilion color through brownish reds to near black, it always shows the bright vermilion color on a fresh surface or by streaking. It contains 86.2 per cent quicksilver and 13.8 per cent sulphur; the specific gravity is 8.0 to 8.2; the hardness is 2 to 2.5; and the sublimation temperature is approximately 580°C. A far less important (though rather common at some mines) mineral is metacinnabarite, a mineral of exactly the same composition but differing in crystal form; this is always brownish black to black in color. Native quicksilver is not at all uncommon, though seldom occurring in quantity in any mine. Cinnabar, metacinnabarite, and native quicksilver are the prime contributors to all mercury production, except that at the Huitzuc mine in Mexico the metal is obtained from livingstoneite, the double sulphide of antimony and quicksilver. At a few other mines the occurrence of the oxide, chloride, oxychlorides, and other rarer minerals, or combinations with some lead or zinc minerals, has been shown.

Cinnabar has been found in many rock types, a factor of considerable importance to the treatment of the ore. Substantial deposits have been found in sandstones, shales, limestone, serpentine, andesite, rhyolite, opalite, and tuff. The variety of host rocks and their differences in physical characteristics and accessory or secondary minerals must be well understood in order to assure efficient treatment.

The most important factor limiting the number of treatment processes is the low sublimation temperature, above which the quicksilver is volatilized and may be recovered by condensation. The fact that this operation may be performed relatively cheaply with an excellent metallurgical recovery and yield a very high-purity metal in one operation puts all combined processes (since they must all eventually roast to make final recovery) at a distinct disadvantage.

Consequently, from the pre-Christian era, the roasting of quicksilver ores has been not only the most popular but, for the most part, the most efficient method of recovery. There have been, however, several other methods used, including a variety of gravity concentration plants, several flotation plants, gravity and flotation combined, and a few chemical plants. These methods are briefly explained, following a description of the more popular roasting methods.

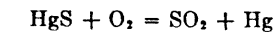
The Roasting of Quicksilver Ores.—The roasting of quicksilver ores depends on raising the temperature to near or above the sublimation temperature of cinnabar, at which point the quicksilver is volatile (as mercuric sulphide vapor) and subject to condensation and collection. The process, therefore, is divided into two distinct operations, *i.e.*, (1) volatilizing the quicksilver and (2) condensing and collecting it. The furnace or retort and the condenser, therefore, are the principal items of equipment, although more or less auxiliary equipment is required to complete the operation and will be discussed in their order.

Retorts.—The retort is the simplest form of recovery plant for treating quicksilver ores, and inasmuch as it requires in addition only a simple condenser and simple firing equipment, it will be described as a complete unit. Retorting is distinguished from furnacing in the fact that retorted ore is heated indirectly, whereas furnaced ore is heated directly with the gases of combustion.

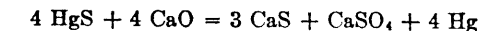
The popular retorts treat one batch of ore at a time in a cast-iron pipe of various shapes. The ore, upon heating, gives forth its mercuric sulphide vapor from which the sulphur must be oxidized to permit the subsequent cooling and condensation of the volatile quicksilver. In most operations, air is depended upon to supply the necessary oxygen and is supplied to the inside of the retort by either natural or induced draft. In the former case, the air circulates by convection, in through the condenser pipe over the bed of ore and out through the same condenser pipe. In the latter case,

the air is usually blown in through the end of the retort opposite to the condenser-pipe outlet, from which it travels over the ore and out the condenser pipe. Other designs of continuous-operation retorts often depend on leakage of air through an ore seal to provide sufficient air for the oxidation of the sulphur.

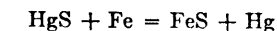
Under these conditions, the chemical reaction taking place is



In treating some ores containing relatively large amounts of sulphur as in high-grade ores, ores containing considerable amounts of pyrite, marcasite, stibnite, etc., it is sometimes desirable to add a flux to assist in the oxidation of the sulphur. This may be lime or iron filings or scrap, the former being more commonly used. When such a flux is used, the reaction is



or



The addition of such a flux is quite necessary in high-sulphur ores in order to free the volatile quicksilver. It is not uncommon, in an improperly ventilated or underfluxed retort operation, to find the formation of synthetic cinnabar, often as long acicular crystals, in the condenser pipe. Similarly, free sulphur may also be deposited and cause additional difficulties in cleaning up the product.

Because the retort is simple, there have been numerous designs. Retorts were one of the earliest devices used for the recovery of quicksilver. Duschak and Schuette[3] report that clay retorts were used at the Idria mine until 1641, when metal retorts were first used. Modern retorts, however, include three general types, each varying according to the manufacturers, who are often the small operators.

The D retort consists of a cast-iron body designed to be set horizontally and on the flat side of the D, *i.e.*, \sqcap . The common size is 20 in. across the bottom by 12 in. high and 8 ft. long. Wall thickness is $1\frac{1}{4}$ to $1\frac{1}{2}$ in. It is closed at one end, and the other end is flanged to take the head, which adds another foot to the length and contains a side exit with flange for a 4-in. cast-iron pipe. The head bolts to the body of the retort and is provided on the front with a recess to accommodate a cast-iron door, securely held in place by a yoke and screw or iron wedges. The heads can be built with either right- or left-hand exits so that they may be set side by side in pairs. To the flanged exit, a cast-iron pipe usually 4 ft. long starts the condenser. To the end of this pipe, set on a slight downward inclination, is screwed or flanged a 4-in. iron cross, and another 4-in. pipe about 8 ft. long inclines downward but parallel to the body of the retort. The other two outlets in the cross are plugged but provide outlets for cleaning. This piping constitutes the average condenser; however, the long condenser pipe may discharge into a concrete box, a system of small tanks, or other devices deemed necessary by the operator to increase the efficiency of his condenser. The condenser pipes are air-cooled or may be water-cooled by dripping water on sacks laid over the long pipe or by more elaborate systems of water-jacketing the pipe.

The retort body and head are set up in a brickwork about 5 × 10 ft. in plan, the bottom of the retort being about 3 ft. 3 in. above the working floor. For heating, a firebox is built into the brickwork at the end opposite the retort door and condenser-pipe outlet and under the retort. The firebox may be designed for wood, fuel oil, or other fuels. A small flue leads the gases of combustion from the firebox toward the feed end of the retort, and at the head two vertical flues carry it upward to the elevation of the retort. It then travels back over the top of the retort body to the fire end of the retort, thence vertically upward through a stack. It is common practice to

use 3 to 6 in. of firebrick, tile, or sand insulation between the lower flue and the bottom of the retort body to protect it from excessive heat, but on the return the bare retort is exposed to the gases of combustion. Although the usual retort body and head are made of cast iron, they have been successfully made of chromium iron with varying chromium content. These have the advantage of resistance to corrosion by the sulphurous gases, as well as oxidation, and are better able to withstand overheating without damage.

In operation, the ore or other material is usually, but not always, charged in three or four steel pans to facilitate charging and discharging the material. Material charged should not exceed $1\frac{1}{2}$ to 2 in., and on finer material the capacity must usually be decreased or the burning time lengthened. On relatively clean ore without excessive fines, a charge of 750 to 1000 lb. can be charged to the retort every 12 hr., giving it a daily capacity of $\frac{3}{4}$ to 1 ton per 24 hr. If they are set up in pairs, the unit would have double this capacity. Although a few retorts have been equipped with thermometers, they are usually operated by observation through peepholes in the brickwork, the retort being kept at a dull red heat by manipulation of a damper in the stack. Operating in this manner usually consumes about $\frac{1}{2}$ to $\frac{3}{4}$ of a cord of wood or 25 to 35 gal. of fuel oil per day. These quantities are subject to variation in operation, character of wood fuel, and character of material being treated. If oil-fired, the burner usually consists of a relatively simple oil burner of the low-air-pressure atomizing type, or an oil mantle burner.

The cost of the ironware described above, plus steel buckstays for the brickwork, stack and fire door and frame, for a double unit is approximately \$1200. About 3250 common red brick and 4000 firebrick are used in setting up a double-D retort. Together with oil-firing equipment, the estimated cost of such a unit is \$2500 to \$3000, depending on location, etc.

The Johnson-McKay type of retort consists of a battery of round cast-iron pipes, usually 12 in. in diameter by about $6\frac{1}{4}$ ft. long. Although the standard setup usually included 12 pipes, they have, in various installations, ranged from one pipe up to a dozen or even more. They have, likewise, been made of pipes of varying dimensions; however, in principle they conform. The pipes are set horizontally and like the D retorts are closed on one end except for a hole to receive a 3-in. condenser pipe, 8 ft. long, which inclines downward. The front end of the pipe includes a bell with a double shoulder to receive two lids which are luted in place with mud or wet ashes, the outer door being more securely held in place, usually by a bar and wedges. The condenser pipes are most often cooled similarly to the method described for the D-retort condenser pipes.

The pipes are supported in a brickwork which, however, is quite different from the D-retort structure. In the D retort the heat passes from the back of the retort to the front, up and back over the top of the retort to the back, and out through a stack. In this type of retort, a firebox is built at one side and for the length of the pipes and the heat passes through several flues under the pipes and at right angles to them for as many pipes as there are in the unit; it then rises to an elevation above the pipes and returns over them to the upper part of the firebox where it is exhausted through a stack. Similar practice is followed in protecting the lower part of the pipes by insulation from the lower flues, although the upper portion of the pipe is exposed to the direct heat.

In operation, the ore is charged by long-handled scoop shovels directly into the pipe and discharged by hoeing out the burnt ore. From 250 to something over 300 lb. of ore can be charged to each pipe, thus giving a 12-pipe unit a capacity of about $1\frac{1}{2}$ to 2 tons per 24 hr., charging each pipe twice a day. This is usually performed by charging one pipe each hour, making two cycles per day. The wood consumption

is roughly 1 to $1\frac{1}{2}$ cords per day, so that by comparison with the double D retort, approximately twice the amount of fuel is required. This is easily understood in the more compact construction and the use of larger pipes in the D retort.

Except for installations of one, two, or possibly three or four pipe units, no retorts of this type have been built in recent years, so that estimates of cost might be rather inaccurate; in any event, it would considerably exceed the cost of the more popular D retort. The smaller installations that have been made have often been cheaply and poorly built and represent only an attempt to "get by cheaply."

A third type of retort, which though very much underdeveloped has been popular during the past few years for prospecting or for small operations, is the inclined-pipe retort. It has been built in a variety of sizes and by nearly as many designers as there are users; however, they are all similar in principle. Most of the units have been constructed of pipes, either cast iron or standard steel, ranging in diameter from about 10 to 16 in. and in length from about 6 to 12 ft. The pipes are set up on a 45-deg. incline and are fed at the top and discharged at the bottom, the discharge being accomplished by raising a door and allowing the material to slide downward through the pipe. Although practice varies, an ore charge is usually left in the pipe for 8 to 12 hr., then the whole charge is withdrawn and a new batch fed in through the top. Feeding at the top of the pipe may be by hand shoveling or by chute from a small ore bin, and the top seal usually consists of an iron plate luted to the pipe with clay or wet ashes.

Near the top of the pipe, a condenser outlet pipe 2 to 4 in. in diameter is cut into the pipe to provide for the exit of the quicksilver vapors, and because air is admitted through an ore seal at the lower end of the pipe, the gas volume (air) through this type of retort is usually considerably more than in other types of retorts. Consequently, more elaborate condensers are used and usually have consisted of various styles of piping of small diameter (2 to 4 in.) with wooden barrels, tanks, or other settling chambers interspersed.

Because of the slope given to the pipe and the fact that this feature lends itself to construction on a side hill, this retort has often been referred to as the "side-hill retort." They are often built in multiple units up to four in a group and are so designed that a masonry pier supports the upper and lower ends of the pipes. Side walls with one or more arches of clay, rock, or brick, over the pipes, provide a shell around all the pipes, and a grate is built behind the lower pier and under the pipes. Fuel of all types has been used, and the heat circulates up and over the pipes to the upper end of the pipes, where it is allowed to escape to a damper-controlled stack.

By their very design, this type of retort is capable of a greater capacity than the horizontal-pipe retorts; however, the absence of good design in the firebox and enclosing shell has resulted in poor distribution of heat with consequent reduced capacity or, more often, incomplete roasting of the ore and reduced recovery. The variety of sizes and designs precludes the possibility of making accurate cost estimates on this type of retort, although they have mostly been cheap installations. If designed and constructed with the same care and materials as are used in the other types mentioned, it seems probable that their cost per unit of capacity would be about the same. Fuel consumption is high, although this might be materially improved with sound design.

Although these three types of retorts represent the most commonly used types, there are many others ranging from pot stills to single and multiple rotary retorts of elaborate design. Few, if any, of these have gained as much favor or stood the test of operation as well as the types described above.

The retort, as has been shown, is a small reduction plant, high in cost per unit of capacity; although subject to many variations, it can be made to operate quite

efficiently. An objectionable feature of all retort operations is the manual charging and discharging operation, which causes exposure to quicksilver fumes. Many arrangements and many devices including hoods, blowers, lids, respirators, and other protective devices have been tried, but the retort continues to subject the workman to the fumes, causing salivation. The substantial portion of production is made in the larger furnace units, but there will probably always be a place for the retort. They are cheaply installed by the small operator, either as a production unit or as a prospecting tool; they are used occasionally by the furnace operator to assist in cleaning up mud and soot; or they are used to retort concentrates from milling operations. In the chemical field, they have a very definite place in the recovery of secondary quicksilver from scrap or in reclaiming the metal from mercurial salts.

Furnaces.—The treatment of quicksilver ores in furnaces differs from retort operation, as previously stated, in that the heat is applied directly to the ore and the gases of combustion are combined with the volatile products liberated by heating the ore. In contrast to retort operation, where only a small amount of air is available for oxidation of the sulphur, furnace or direct-fire treatment of the ore makes available larger quantities of air. The amount available as excess over requirements for combustion of the fuel, therefore, is of extreme importance. It must provide sufficient oxygen to combine with all the sulphur released by the cinnabar or other sulphides which may dissociate within this temperature range and to combine with certain other volatile elements such as arsenic or antimony. Any larger quantity only requires additional fuel for heating and increases the volume of gases to be handled. In practice, it is necessary to maintain an excess over theoretical requirements in order to assure contact and a sufficient volume for sweeping the quicksilver vapors from the furnace. In addition to this difference, furnace treatment usually infers greater capacity and continuous operation.

Although it was probably not the first furnacing operation, as above defined, López Saavedra Barba is given the credit for inventing, or at least first applying, the shaft type of furnace to the treatment of quicksilver ores. This was in 1633 at the Santa Barbara mine in Peru. The success of this type of furnace led to its introduction at the Almaden Mine in Spain by Bustamente, where a number of them were built within the next twenty-five years. They have since acquired the name Bustamente furnace, and many of these original installations, now 300 years old, are still in use.

Furnaces built up to 1916 (with only a few exceptions thereafter) are generally referred to as the "brickwork furnaces," because of the massive brickwork necessary to contain them. Since that time, the "mechanical furnaces" have taken over and are today the only type in use.

The brickwork furnaces were of several designs, originating probably with simple shaft furnaces. This design was later modified, and the shelf or tile furnaces became more popular owing largely to the requirement for treating fine ore. A tabulation of furnace types follows:

Brickwork furnaces

1. Intermittent type.
 - a. Simple shaft furnace.
 - b. Bustamente, invented in Peru, 1633, and developed at the Almaden in Spain.
 - c. Neat.
2. Continuous type.
 - a. Exeli, developed at Idria, 1872.
 - b. Knox-Osborn, developed in California from 1872.
 - c. New Idria Coarse Ore, developed at New Idria, 1900.

- d. Spirek, developed at Idria about 1910.
 - e. Kroupa, developed at Idria about 1915.
3. Shelf or tile furnaces.
 - a. Knox & Osborn, developed in California, 1870's.
 - b. Huttner-Scott, more popularly called the Scott, developed at New Almaden, 1875.
 - c. Cermak-Spirek, developed at Idria, 1886.
 4. Side-hill furnaces.
 - a. Livermore.
 - b. Fitzgerald, more properly a large side-hill retort.

Mechanical furnaces

1. Rotary furnace, developed at New Idria, 1916.
2. Multiple hearth furnace, developed at New Almaden, 1916, more popularly referred to as the Herreshoff.

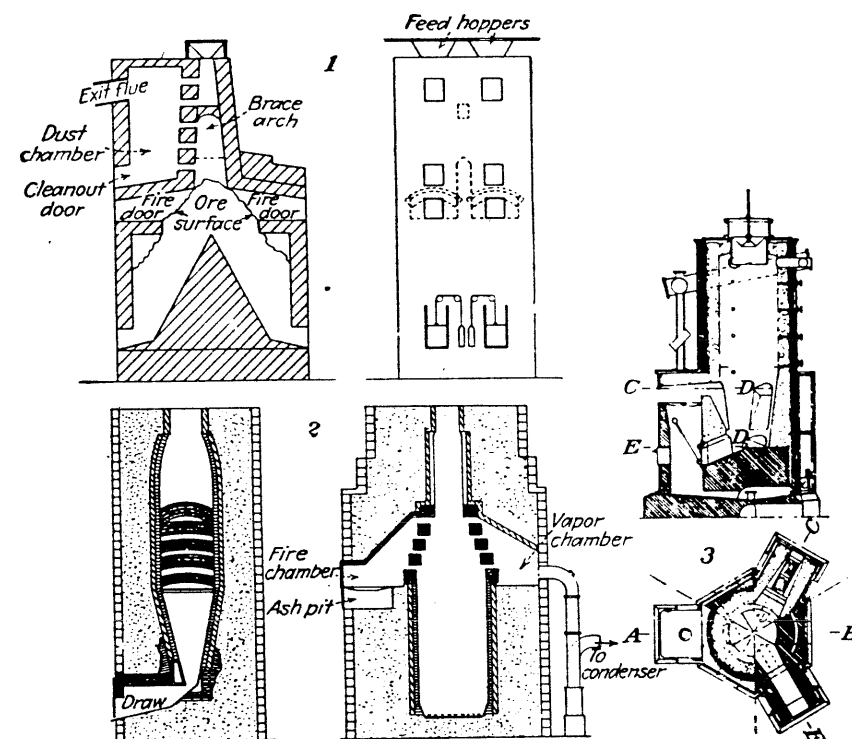


Fig. 1.—Coarse-ore furnaces: 1, New Idria type; 2, Knox & Osborn; 3, Exeli iron-clad.

While this is not a complete list of all furnace types, it represents the more soundly designed furnaces and those which have a production background. It represents the plants used not only in the United States but also in Spain, Italy, and other quicksilver-producing countries of the world.

Furnaces listed under Brickwork furnaces, 1, 2, and 4, were all designated as coarse-ore furnaces. All those under 1, also 2d, contained their fuel within the ore charge, and in those of the intermittent type the furnace was charged with a layer of ore and a layer of fuel until filled, the charges fired, and it was allowed to burn out.

The gases containing the quicksilver vapor were drawn off the top into condensers (to be discussed later under that heading). After the fuel had burnt out, the furnace was

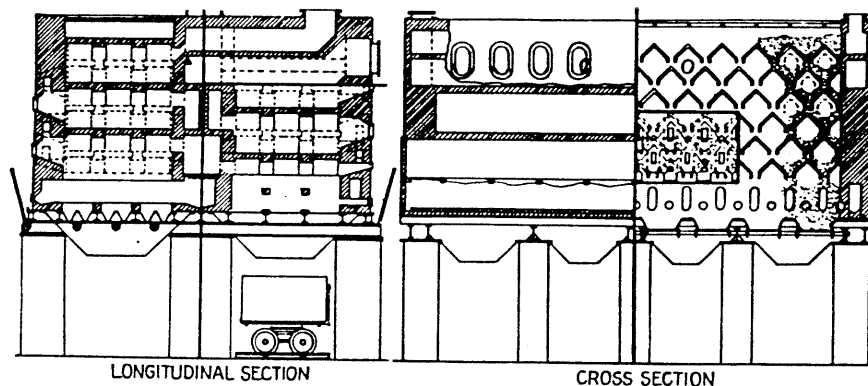


Fig. 2a.—Fine-ore furnace (Cermak-Spirek).

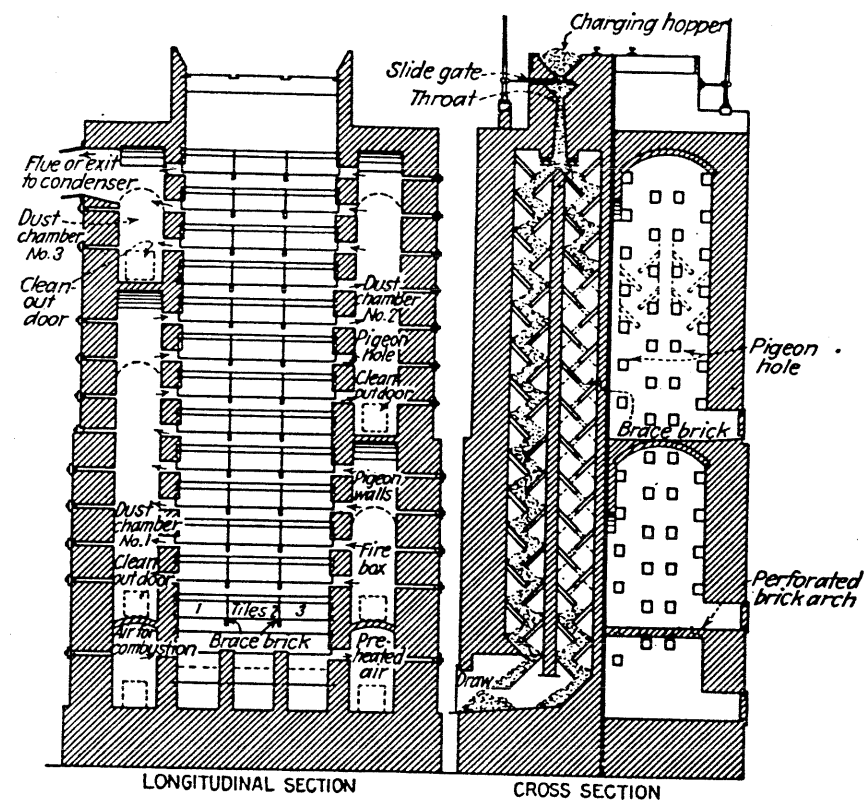


Fig. 2b.—Scott shelf furnace.

allowed to cool, the charge withdrawn, and the shaft recharged. Cuts of these furnaces are shown in Figs. 1, 2, and 3.

The change to the continuous-type furnaces in the '70's was required in order to gain greater capacity for the treatment of lower grade ores and the large demand for quicksilver for amalgamation by the gold-producing industry (in the United States). Although considerable change in design was required, the principle remained the same as in the earlier shaft furnaces. For the most part, it meant arranging suitable gates, rakes, or doors for intermittently drawing off a portion of the roasted ore, providing for suitable charging doors at the top of the furnace, and adding a firebox, either near the bottom of the furnace or part way up (New Idria coarse-ore furnace), as most of these furnaces depended on the application of heat from an external source. Kilns of the shaft type as under 1 and 2, being made of heavy brick walls and requiring a minimum gas-volume travel through the charge, had relatively high thermal efficiencies but were not suitable for larger capacities. For best operation, the ore had to be all coarse; else the fines would fill the interstitial openings and blind off a section of ore from heating. This feature together with a requirement for a relatively dry feed, in part, led to the development of the shelf or tile furnaces listed under 3.

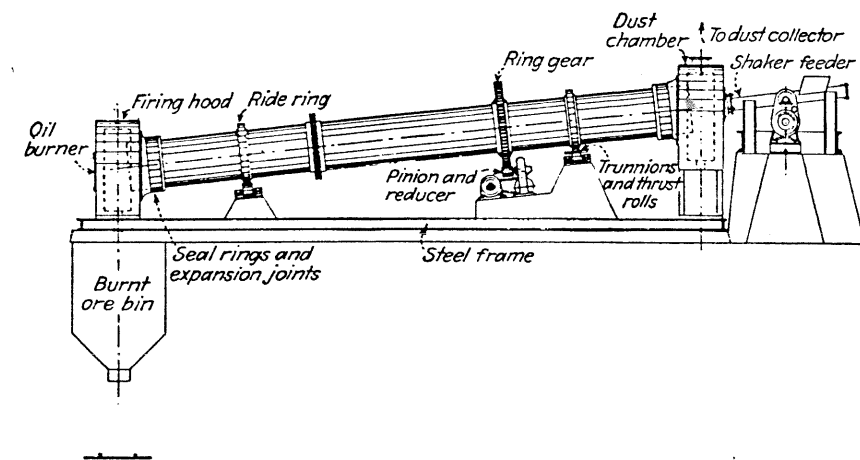


Fig. 3.—Rotary furnace

The three furnaces, here listed, are all known as fine-ore furnaces and, in addition to the reasons just pointed out, were developed because of the need for a furnace to treat the fine ore made in blasting for larger scale production. It was the custom at the older plants, where only coarse-ore furnaces were installed, to make adobes of the fines produced in cobbing or sorting. The adobes were made by mixing the fines with local mud into bricks (several sizes, though mostly about the size of a common brick) and sun-drying them. As the quantity of fines increased, this obviously became an expensive procedure, and there developed the need for a furnace to treat fine ores.

Although there was reputedly no collaboration or connection, one with the other, the three furnaces utilized the same principle in permitting ore to pass downward through a shaft furnace thus keeping it from packing, to prevent blinding. This was accomplished in the Knox-Osborn and in the Scott by feeding the ore at the top of the furnace into one or more shafts, in which tile set at an angle of 45 deg. and staggered was set in the side walls. The ore pursued a zigzag course downward from one tile to the next, the tiles being set 3 to 6 in. from each other at the edge. Peepholes permitted observation of the course of the ore as well as rabbling, should it hang up between tiles.

The essential difference between the Knox-Osborn and the Scott was in the firebox and the course of the hot gases through and over the ore. In the Knox-Osborn, a firebox the height of the shelf system was built on one side of the furnace. The gases traveled horizontally across the furnaces, under the tiles and over the ore, to two chambers on the opposite side. In these, the dust settled and the gases, including the quicksilver vapor, were drawn off. In the Scott furnace, a low firebox on one side was used. Hot gases from the firebox traveled across the furnace, as in the Knox-Osborn, but only under the bottom two or three tiles. At the opposite side, a chamber received these gases and reversed their direction so that they again traveled across the furnace, but in the opposite direction and the next two or three tiles higher. There a similar chamber again reversed the direction for heating higher tiles, and so on, depending on the height of the furnace. At the top, the gases leave the furnace for the condensing system.

The Cermak-Spirek furnace, developed at the Idria mine in 1886, is similar to the above two types as to ore flow except that, instead of the flat tiles used for changing the direction of the ore, a pyramided arrangement of gable tiles accomplishes the same purpose. In regard to heat flow, it is similar to the Knox-Osborn and, unlike either furnace, it is usually built lower and with more tiles.

Mechanical Furnaces.—The previously described furnaces are distinguished from the so-called "mechanical furnaces" largely by the lack of machinery required in their operation. About the only mechanical equipment required (and it was not always used) was an exhaust fan for drawing the quicksilver-laden gases from the furnace and through the condensing system and, at the same time, creating an adequate draft over the firebox for good combustion.

The development of mechanical furnaces was possibly delayed (by comparison with the mechanization of other metallurgical processes) because of two principal factors: (1) the brickwork manually operated furnaces made an excellent recovery when properly operated; and (2) the average quicksilver operation was small, subject to wide fluctuations of the market, and, consequently, usually not financially able to experiment with more expensive and complicated equipment.

In 1916, under demand created by the Second World War, it became apparent that larger tonnages of lower grade ore would have to be treated. It would not have been feasible to attempt to increase the size of the then popular Scott furnaces, and the break away from the brickwork furnaces began.

Although various types of mechanical furnaces have been built, the successful types are the rotary furnace and the multiple-hearth type furnace.

The rotary furnace is by far the most popular type in present use and has gained this popularity largely through its low initial and operating cost, its great flexibility and ease of control, and in most cases by considered design by the manufacturer to meet conditions encountered at the individual mine.

Three early attempts were made to apply the rotary furnace to quicksilver ore reduction although it was suggested as early as 1876. The first attempt was made at the Socrates mine in California in 1903, the second at the Aurora mine in California in 1911, and the third at the Abbadia San Salvatore mine in Italy in 1913. Of the first two operations, little is known; however, their failure to remain in operation probably indicates their lack of success. The Italian operation has been well described by Duschak and Schuette[3], who outline the difficulties encountered and later overcome to a certain extent.

The beginning of the rotary furnace, however, may be dated from 1916 at the New Idria mine in California. At this property, an experimental furnace was installed in that year, and in the year following four larger furnaces were installed. The

successful operation of these furnaces led to their further development and many subsequent installations.

The multiple-hearth type furnace was first applied to quicksilver ore reduction also in 1916 at the Senator mine in California and the Goldbanks mine in Nevada. Furnaces of this type, known as the McDougal, Herreshoff, or Wedge furnaces, had been successfully used in many other types of roasting operations so that the application to quicksilver ore reduction was mostly a matter of adjustment of operating conditions rather than a change of basic design.

In both types of mechanical furnaces, a continuous flow of ore passes through the furnace, and while the ore is in the furnace, it is continuously moved, agitated, or stirred. This brings all particles into direct contact with the hot gases of combustion and permits the quicksilver vapor to be quickly drawn from the furnace atmosphere. In contrast to the brickwork furnace, ore remains in the furnace only 30 to 90 min., as compared with 6 or 8 hr. up to several days. Nearly complete extraction of the quicksilver from the ore is obtained by roasting the ore above the sublimation temperature of cinnabar and by providing sufficient air to oxidize the sulphur quickly.

Rotary Furnaces.—The rotary furnaces used in quicksilver-ore-reduction plants are of the familiar cement-kiln type. They include a slightly inclined steel shell supported and rotated on two riding rings, or tires, and driven through a pinion by a ring or girth gear fastened to the shell. The riding rings revolve in trunnions and are usually spaced so that the weight of the shell is distributed evenly. The ring gear and drive is usually near the upper ride ring, although this practice is not universal. At each end of the shell, it is necessary to provide gas seals in order to prevent the leakage of quicksilver vapors outward or an inward leakage of cold air. The seals permit the shell to rotate in the stationary hoods at each end of the shell, usually referred to as the firing hood and the dust chamber. The ore is fed to the upper end of the shell by any of several types of feeders, and as the shell rotates the ore rolls and slides downward to be discharged at the lower end.

In usual practice, kilns are counterflow, *i.e.*, the ore is fed in at the upper end and the burner is placed at the lower end so that the gases of combustion and the volatile constituents of the ore travel counter to the flow of the ore and are drawn from the kiln at the upper end. There are, however, a few exceptions, which are later described, in which the kilns are parallel flow. In this arrangement, the ore is fed to the kiln and fired at the upper end and the ore is discharged and the gases withdrawn from the kiln at the lower end.

Rotary-furnace plants are usually rated by the size of the shell, with all other equipment being sized proportionately. The tonnage capacity bears a definite relation to the size of the shell used, although such factors as moisture content of the ore, size and character of the ore, sulphur content (as cinnabar, free sulphur, or other sulphides), and type of fuel used, all influence capacity. One manufacturer[4] lists the following standard sizes, with average range of capacity for each size:

STANDARD SIZES OF ROTARY KILNS

Diameter, in.	Length, ft.	Tons per 24 hr.
21	18	8-12
24	24	12-25
36	40	25-40
36	48	40-60
48	64	60-100
60	84	100-150

There have been kilns of many other sizes built; however, the sizes shown have been accepted as suitable under most circumstances. A typical layout for the 24 in. X 24 ft. size, together with other required equipment, is shown in Fig. 4.

The shells are constructed of rolled steel plate ranging from $\frac{1}{4}$ in. thickness for the smaller sizes to $\frac{1}{2}$ in. in the largest. Riveted construction is most common, although several all-welded shells have been used.

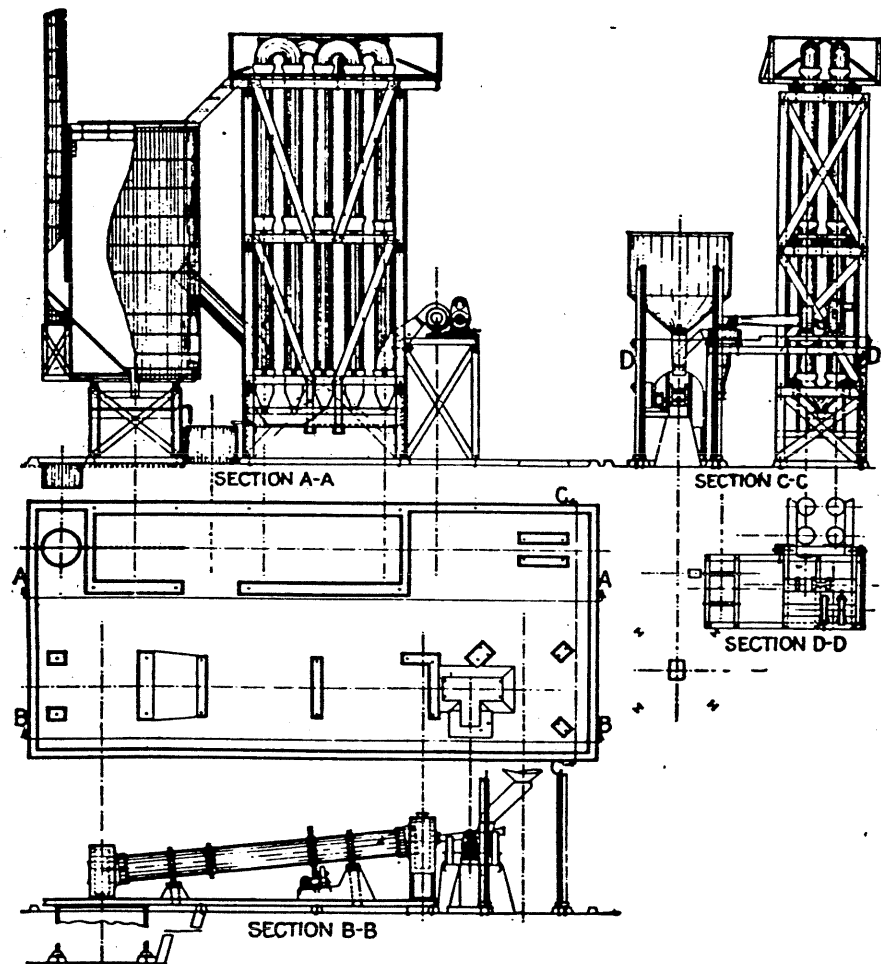


FIG. 4.—Layout of 12- to 25-ton rotary-furnace plant.

In order to protect the shells and as insulation, they are always lined with firebrick or other refractory material. In the standard-size kilns, standard $4\frac{1}{2}$ -in. arch brick are usually used, thus giving an inside diameter 9 in. less than the shell diameters listed. Standard 6-in. cupola blocks are used in the 60-in. diameter kilns. Because of the difference in the abrasive nature of various ores, it is difficult to give an average brick-life figure; however, it will probably range from 1 to 5 years of continuous operation. Lining is a relatively inexpensive and simple operation that can be

accomplished in 2 to 5 days, including cooling and starting-up time, depending on the kiln size. In order further to insulate the shell and gain greater fuel economy, most brick linings in rotary kilns are rested on asbestos sheets between the brick and the shell. This material, 1 in. thick and 24 X 36 in. in size, keeps the shell temperature considerably lower and also cushions the brick, thereby prolonging their life.

The inclination of the shell varies from $\frac{1}{2}$ in. per ft. in the largest size to $1\frac{1}{4}$ in. per ft. in the smallest size. Variations are made not only as to kiln size, but also to assist in adjusting the depth of the bed of ore in the kilns. This is also accomplished by variation of the speed of rotation, which ranges between 30 and 90 sec. per revolution. The kilns are driven by an electric motor, through V-belt drive to a worm or herringbone speed reducer and pinion to the ring gear. Motors installed range from 1 to $7\frac{1}{2}$ hp. with about one-half the installed horsepower being required for operation.

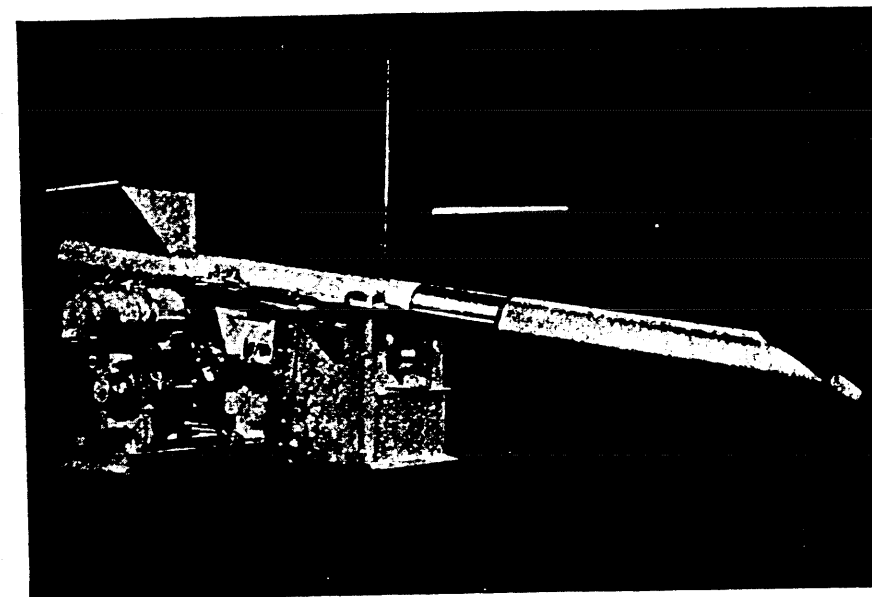


FIG. 5.—Shaker feeder (8-in.).

The seal rings (and expansion joints), located at each end of the shell, are of a number of types. A tight seal is necessary, although pressures seldom exceed $\frac{1}{4}$ in. of water, in order to prevent fume leakage or an inward leakage of cold air which would tend to condense quicksilver within the kiln or in the flues before reaching the condensing system.

The firing hood, a brick-lined steel hood at the lower end of the kiln, contains the burner equipment and also provides for the disposal of the roasted ore into a bin or hopper below floor level. The dust chamber at the upper end of the kiln derives its name from early practice, when this was a large chamber, usually with baffle walls, in which the gases from the kiln were supposed to drop their dust by reduction in velocity and while still hot enough to prevent condensation of the quicksilver. The development and application of dust-collecting devices have reduced the dust chamber to a small, simple header for the kiln.

Through the dust chamber, the ore is fed into the kiln. The feed to rotary kilns is never sized, and in kilns of the larger sizes, up to 3-in. material can be roasted with satisfactory extraction. The size is largely controlled by the feeder, and for the

smaller-size kilns, material up to 1½ in. is successfully handled. The most satisfactory feeder for handling all types of ore, unsized, wet or dry, is the shaker feeder shown in Fig. 5. The feeder, driven by motor through a variable-speed reducer, has a wide range of capacity and is mechanically simple. The ore is fed into the hopper by gravity, and the feeder tube, ranging from 5 to 10 in. in diameter, resting on rolls or slides, is carried back by the rotation of the cam. At its point of maximum backward travel, it is released by the cam, and springs pull the pipe forward against a bumper block, causing the ore to slide ahead in the pipe and on into the kiln. A range of 30 to 90 r.p.m. of the cam and variable spring tension provide for easy adjustment to various operating requirements. Where the feeder tube extends through the dust chamber into the kiln, a seal must be provided to prevent leakage of fumes. This has been successfully accomplished by using a glass-cloth diaphragm attached to the feeder tube and to the dust chamber. Motors installed for operation of the feeders range from 1 to 7½ hp., and one-fourth to one-third of the installed horsepower is required for operation.

Firing Rotary Furnaces.—Most American rotary-furnace installations have used oil for fuel; however, wood, coal, butane, and natural gas have been used. Butane and natural gas have the advantage of providing a clean fire, easily controlled, but cost usually precludes their use. Coal has not generally been used because of the availability of other fuels and the fact that in order to obtain best results from this fuel the more expensive equipment required for powdered-coal firing is required. Wood has been used successfully at a number of installations where it was available and the transportation of other fuels was costly. It is more difficult to maintain uniform temperature using wood fuel, and the greater volume of gases of combustion reduces the capacity of the plant materially.

Oil firing, consequently, is by far the most popular, and lends itself well to flexibility, ease of control, and economy of operation. Fuels ranging from 12 to 33°Bé. are used, the higher gravity oil usually being used in the smaller plants because of its greater flexibility. It is of prime importance that, whatever fuel is used, good combustion must result in order to prevent the accumulation of soot or tars in the condensing system together with the collected quicksilver. Such soot or tars make the separation of the quicksilver far more difficult, as will be described under Soot Machines.

Oil firing of rotary furnaces has been accomplished in both low-pressure and high-pressure burners, the latter predominating. In either type, the burners are mounted on the firing hood and extend toward or into the lower end of the kiln. In most operations, the lower end of the kiln acts as the combustion chamber; however, some firing hoods have been constructed to contain the mixing chamber, ignition block, and combustion chamber, with only the hot gases of combustion entering the kiln. Considerable progress has been made in recent years in the better design of burner equipment and its application, resulting in better fuel economy. Air is used for atomization, and various schemes have been utilized to preheat the oil and air. The oil is usually preheated in a thermostat-controlled electric oil preheater, whereas the primary and secondary air are most often preheated by the utilization of the waste heat in the burnt-ore bin.

If the high-pressure type of burner is used, air at 40 to 100 lb. per sq. in. must be supplied and requires 3 to 25 hp. through the standard sizes of kilns. Oil is usually (though not always) supplied at similar pressures and requires ¼ to 1 hp.

While the consumption of oil varies in accordance with the character of the ore, moisture and sulphur content, size of kiln, and percentage of capacity at which the kiln is being operated, it will range between 4½ and 8 gal. per ton (see later discussion of parallel-flow kilns) and probably average about 6½ gal. per ton.

Although low-pressure burner equipment has been used successfully at a number of installations, it is generally conceded not to be so satisfactory as the high-pressure type when firing a dusty ore. The first cost of low-pressure equipment is equal to or greater than high-pressure equipment, and although power requirements are a little less, oil consumption is usually greater.

Multiple-hearth Furnaces.—Multiple-hearth furnaces consist of a cylindrical metal shell that supports conical or spherical arches of firebrick decked one above the other. A vertical central shaft running through the center of the brick arches carries rabble arms on the various decks, which on rotation rakes the ore across the decks. The feed is at the top, either at the center or on the periphery of the shell, and the ore is raked first outward, then inward, as it drops through ports to the deck below. (The raking action would be reversed depending on whether the feed started at the center or on the periphery.)

The Herreshoff furnace, which is the most commonly used multiple-hearth furnace, is shown in Fig. 6. This furnace is manufactured[5] in a number of standard sizes as follows:

Outside diameter of shell	Number of hearths	Tonnage capacity per 24 hr.
36" (i.d.)	8	2
10' 0"	4	20
10' 0"	6	30
13' 6"	6	50
16' 0"	6	75-100
14' 3"	13	125

The 36-in. size has been successfully used as a laboratory or testing unit and also as a unit for treating concentrates produced by wet-concentration methods. The 13-hearth unit is a new "three-zone furnace" which is described later.

The hollow central shaft is carried on heavy bearings and is rotated by a bevel gear at the bottom, further reduction being obtained by a gear-reduction unit. The speed of rotation of this shaft normally ranges between 45 and 60 sec. per revolution and is determined largely by the period of contact required (or capacity) or the depth of bed of ore on the hearths. The power required is 2 to 3 hp. in the various sizes. The central shaft is hollow in order that cooling air may be blown through an inner pipe, out through the rabble arms, and back into the central shaft outside the inner pipe. The air is either vented at the top of the central shaft or piped back to be used as preheated air in the hearth areas. The power required to provide this cooling air is approximately 3 hp. Notable improvement has been made in the adaptation of heat-resisting metals for the construction of the rabble arms and raking teeth to give them greater life. With adequate air-cooling and design to permit easy access, these items may be changed with very little lost time.

The ore is fed at the top of all furnaces of this type so that the ore must be elevated. This is commonly accomplished through the use of bucket elevators or belt conveyers which discharge into a small surge bin built directly on top of the furnace. From this bin or hopper, the ore drops onto a shelf above the top hearth, from which it is "wiped" off by a feed knife attached to the top rabble arm. The speed of rotation of the central shaft or the pitch of the "wiper" governs the rate of feed.

In order to maintain a uniform bed on each hearth, it is necessary that the ore should be more closely sized than required in rotary-furnace operation; 1¼ in. is

about the maximum size treated. In some of the smaller plants this is reduced to $\frac{5}{8}$ or $\frac{3}{4}$ in.

As the ore travels downward from hearth to hearth, it is thoroughly stirred and exposed to the hot gases of combustion and is finally discharged through a port in the bottom hearth to a burnt-ore hopper under the furnace or directly into a car for tramping away from the furnace.

In the operation of all multiple-hearth furnaces, it is common practice to use one or more of the top hearths for drying or preheating the ore, then dropping onto the next one or more hearths for the roasting of the ore, and finally dropping onto one or more hearths for soaking and cooling before it is finally discharged.

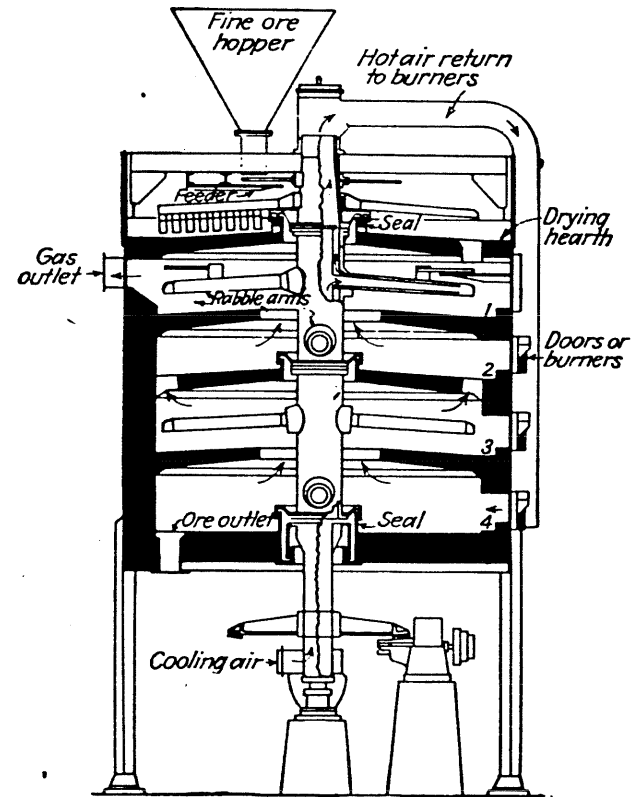


FIG. 6.—Diagrammatic sketch of Herreshoff furnace.

Firing Hearth Furnaces.—Multiple-hearth furnaces, in fields other than quicksilver, have been fired with all fuels; however, as applied to quicksilver, they have, in all but one installation, used oil. The exception used wood at first and finally one-half wood and one-half oil.

Because of the classification of the hearths into drying, roasting, soaking, or cooling zones, the firing is done through ports in the shell on the roasting hearths. In some of the earlier installations, separate fireboxes were built outside the shell; however, because of excessive fuel consumption, all modern installations fire through the shell and directly onto the hearths. Low-pressure burners, using approximately the same range of fuels as are used by the rotary-furnace operations, are used, and oil con-

sumption varies because of the same factors that influence oil consumption in rotary furnaces. The average oil consumption, however, is slightly higher, probably approximately $7\frac{1}{2}$ gal. per ton.

Three-zone Hearth Furnace.—A recently installed Herreshoff furnace, described as a "three-zone furnace," is of interest in that an attempt has been made to utilize to as great an extent as possible the waste heat in air used to cool the central shaft and rabble arms and the waste heat from the roasted ore[6]. The furnace is 14 ft. 3 in. in diameter and includes 13 hearths, divided into three zones: the drying zone, consisting

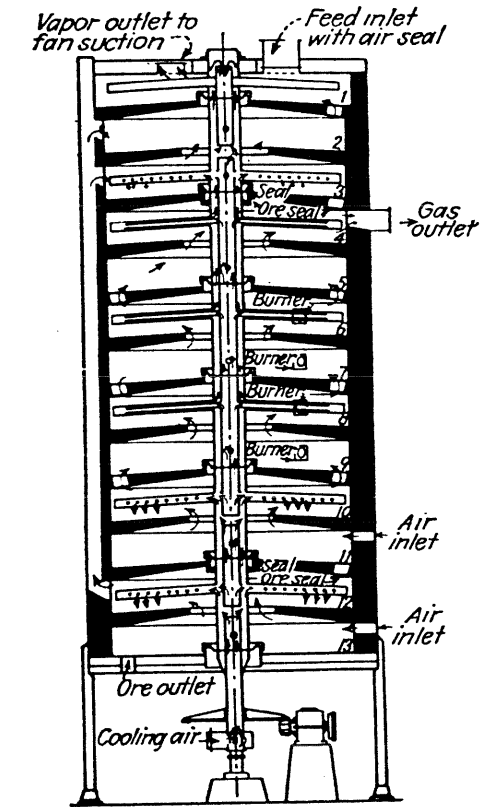


FIG. 7.—Herreshoff three-zone furnace.

of the top three hearths; the central heating zone, consisting of the next eight hearths, the top two being preheat hearths, the next four being burner hearths, and the bottom two being soaking hearths; and the cooling zone, consisting of the two bottom hearths of the furnace.

Figure 7 shows the furnace diagrammatically. Cooling air is forced up the central column and a portion forced out through the rabble arms on the cooling hearths. This portion, together with air admitted through a port in the shell, is drawn off these two hearths through four ducts running to the bottom of the drying zone where it is passed over the wet ore.

Another portion of the central-column cooling air is forced through the rabble arms of the two soaking hearths to combine with additional air admitted through a

port in the shell and provide secondary air for the central heating zone. This air, together with the gases of combustion and volatile products, is drawn off from the top of the central heating zone and sent through a dust collector and condensing system.

Finally, the remainder of the central-column air is forced through the rabble arms of the burner and preheat hearths without escaping to the central-heating-zone atmosphere, and thence through holes in the rabble arms of the top drying zone directly on the ore. In this zone it combines with air preheated in the cooling zone and is drawn from the top of the furnace by a separate exhaust fan and sent to waste.

Substantial fuel savings over the conventional single-zone furnace are reported, and a capacity of 125 tons per day, or more, is obtained.

Because the design of the multiple-hearth furnace requires the installation of a number of brick arches, sprung with a relatively small rise and supported against a circular brick wall within the shell, a variety of brick shapes is required to make a complete lining. Inasmuch as the hearths are largely protected by a bed of ore, there is little abrasive action on the brick by the passage of the ore through the furnace so that brick life, from the standpoint of abrasion, is very good. On the other hand, it is essential that the lining be skillfully and carefully installed to prevent a hearth from sagging or dropping. Likewise, frequent shutdowns and start-ups have a tendency to aggravate this condition and should be avoided.

Comparison of Rotary and Hearth Furnaces.—To compare the rotary furnace with the Herreshoff furnace, it must be realized that in few instances is there an opportunity to make direct comparison on the same type of ore and the same management. At the Bonanza mine in Oregon, the first installation was a Herreshoff, which was followed by two rotary furnaces. After the installation of the rotaries, all ore was screened and the fines roasted in the Herreshoff, the coarse going to the rotaries. The Pinchi Lake mine in British Columbia made an original installation of two rotary furnaces followed by three Wedges. In this operation, likewise, the fines were screened out and fed to the Wedge furnaces. In each of these operations, and it may be generally stated, with proper operation the extraction of quicksilver from the ore may be made equally well in either furnace. Fuel requirements are somewhat higher for the multiple-hearth furnace, and power requirements are possibly slightly higher for the rotary furnace. Although brick wear by abrasion is higher in the rotary, it is doubtful if over-all brick cost is any greater because of the more extensive shutdown required for the occasional repair necessary in the hearth furnace and the more expensive brick required. From the standpoint of general maintenance, the rotary furnace has the advantage. The rotary is simpler to operate and a good deal more flexible than the hearth furnace. Again, in point of initial cost, the rotary has the advantage. It is quite natural, therefore, that rotary-furnace installations have exceeded multiple-hearth-furnace installations by several times.

Flow Sheet of Furnace Plants.—Beyond the furnace, the flow sheets of most quicksilver-ore-reduction plants show a far greater similarity. Notable changes in the equipment beyond the furnace took place about the same time as the development of mechanical furnaces and have been developed with, and because of, the furnace development. This was primarily necessary because of the change of character of the gases evolved from the mechanical furnaces as compared with those of the earlier brickwork furnaces. In the earlier furnaces, many of which operated under natural draft, gas volumes were relatively smaller; because of lack of mechanical agitation of the ore and the smaller gas volumes (and correspondingly, velocity) less dust was carried in the gas stream out of the furnace; a good many of the furnaces predried the ore feed before it entered the furnace (a feature used in part in modern Herreshoff

furnaces), thus reducing water vapor in the condenser gases; and since the development of mechanical furnaces, there has been a substantial reduction in the average grade of ore treated, thus reducing the percentage of mercury vapor in the gas stream.

In the earlier brickwork furnaces, the condensers, therefore, were far simpler—but probably less effective. Dust was not a serious problem and was usually removed from the gas stream by passing the gases through a large brickwork or masonry chamber while they were still hot enough so that the quicksilver would not condense. A reduction in velocity and, at times, baffles, screens, or sprays within this chamber were depended upon to clear the gases of all dust. They then passed into one or several similar chambers, sometimes through a spray of water, for condensation and collection of quicksilver. Although their advantage was simplicity, these condensers had numerous disadvantages: they were more expensive than modern condensers; being built with heavy walls of material of low thermal conductivity, their rate of heat transfer was low and they were necessarily large; the materials of construction would absorb considerable quantities of quicksilver which either would be lost by leakage into the ground beneath them or would be tied up until a portion of this loss could be recovered by "mining" the area under old condensers and the condensers themselves reburned; they presented a difficult cleanup problem in that it was not possible to centralize collection; and they created a very severe health hazard as cleanups frequently meant entry to the chambers for hoeing or flushing out.

The two principal factors, however, that led to improved dust collection and condenser design were the increased amount of dust generated in the mechanical furnaces and the smaller amount of quicksilver in the condenser gases.

Dust Collectors.—Improved dust collection began with the installation of several Cottrell electrical-precipitation units, one on the Herreshoff at the New Almaden mine, and subsequent installations on rotary-furnace plants at the Sulphur Bank mine in California, the Opalite mine in Nevada, and the Arizona Quicksilver Co.'s property in Arizona. At the Sulphur Bank, two Cottrells were installed, one to precipitate the dust, called the "hot-treater," and one to precipitate quicksilver, called the "cold-treater." Although quite effective, their initial cost and high cost of maintenance were excessive and collectors of the familiar cyclone type came into general use.

The use of the first cyclone-type collector at the Knoxville mine in California was followed by its installation at many other plants, and today it is accepted as the most satisfactory unit for either the rotary or multiple-hearth furnace. The more popular type in use is the single-cone type with a fairly large diameter, although several of the multitube type, in which one or more small cones are installed, have been used. Initial cost favors the former, results are about the same, and wear or plugging is against the multitube type.

The quantity and character of dust collected varies over rather wide limits. In quantity it will probably range from as little as $\frac{1}{4}$ of 1 per cent to over $2\frac{1}{2}$ per cent of the feed. In many plants the operation of the fire or condensing system is given more consideration than the operation of the dust collector; however, they seem to function quite efficiently over a range of volumes and temperatures. Cyclones of the Sirocco type are designed to work most efficiently and at reasonable back pressures when the gas enters at velocities of 1600 to 2000 ft. per min. The gases leaving any quicksilver furnace must be kept above the dewpoint; hence the gases entering the cyclone are relatively hot. The temperature will vary according to furnace design and operation as well as the grade of ore (i.e., concentration of quicksilver vapor in the gas stream); however, it will usually range between 400 and 600°F. In the case of the parallel-flow rotary kilns, later described, the temperature of the gas leaving the kiln is considerably higher.

By employing a properly sized collector with flues of such size that velocities are not excessive and by maintaining temperatures above the dewpoint, the dust collected should be very low in quicksilver content. The loss is attributable to finely divided cinnabar carried out of the furnace by the draft and also to condensed quicksilver. Obviously, the amount of cinnabar depends largely on the character of the mineral in the ore: if the cinnabar is finely crystalline or if the ore is mostly fines, there will be a greater tendency for the cinnabar to be carried over than if it is heavily crystalline or the ore coarse. Condensation of quicksilver in the collector is usually caused by cooling of the gases in "dead pockets" within the collector. It has been found that when ores running 8 lb. per ton or less are being treated, the collected dust approximates the grade of ore being treated. As the grade of ore treated increases, the loss increases somewhat but not in direct proportion. Because the dust collected is a small amount, the total loss of quicksilver, either in quantity or by percentage, is usually small and at most operations is discarded. At several plants, however, flotation, blankets, or hydraulic classification has been employed, with varying results, to recover a part of this loss.

Condensing Systems.—The improvement of the condensing system, as previously stated, was largely influenced by the reduction in grade of ore being treated. Economically, there was the requirement that the maximum recovery should be made—a fact that probably was given less consideration when the more profitable higher grade ores were being treated. Metallurgically, the reduced concentration of quicksilver vapors in the gas stream lowered the dewpoint and required condensers of greater heat-dissipating characteristics than were formerly used. This point has been graphically illustrated by Duschak and Schuette[3]. In attempting to satisfy these two requirements, the other disadvantages of the brickwork condensers were also attacked.

The function of a condensing system is to cool the furnace gases to below the dewpoint, at which condensation begins, and then collect the finely divided globules of condensed quicksilver from the condenser atmosphere and structure. The cooling is primarily essential; the collecting should be as simple and complete as possible.

There has probably not been, since 1917 and 1925, as thorough or comprehensive a study made of quicksilver-furnace gases, their condensation, collection, and losses, as set forth in the *U.S. Bureau of Mines Technical Paper 96*[7] and the *U.S. Bureau of Mines Bulletin 222*[3]. The conclusions reached refer principally to condensation of quicksilver-bearing gases from Scott furnaces and in types of condensers now considered obsolete. It is probably true, however, that much of the subsequent thinking was a direct result of the publication of this information and that directly or indirectly many of the findings were applied to new designs. In fact, however, a direct application of theoretical requirements to the design of a condensing system is impractical, if not impossible. The variation of composition of ores and moisture content, the building up of quicksilver soot on the walls of the condensers, the variation of gas volumes and velocities, changes in atmospheric temperature, pressure, and humidity, and the always variable grade of the ore are some of the factors that would have to be considered in design. As a consequence, and with as many of these factors as possible in mind, condensers were designed, in the builder's opinion, to be adequate for the most demanding conditions of the particular installation. Unfortunately, this opinion was not always sufficient. On the other hand, several types have been designed which proved to be efficient when working within their limits, and sizes have been developed to which the builders are willing to assign a capacity, based largely on averaging the above factors against the ore to be treated. When applied conservatively and with experience and when careful and uniform plant operation is obtained, good results are secured more often than not.

In an attempt to improve the cooling capacity of condensers, it was natural that a break from brick or masonry chambers was the first step. Early installations using metal, glass, wood, and chemical stoneware were tried with varying success; however, they were not generally used until the advent of mechanical furnaces. Soon after their introduction, common vitrified sewer tile was adopted in several different types of layouts. The simplest were no more than long flues, usually leading from a brick or masonry dust chamber to a stack. In size they varied, depending on the volume of gas to be handled, and were often in several strings. This type of system was difficult to clean up and scattered the condensing system over quite a length. The next step was in compacting the tile systems into units, mounted from nearly hori-

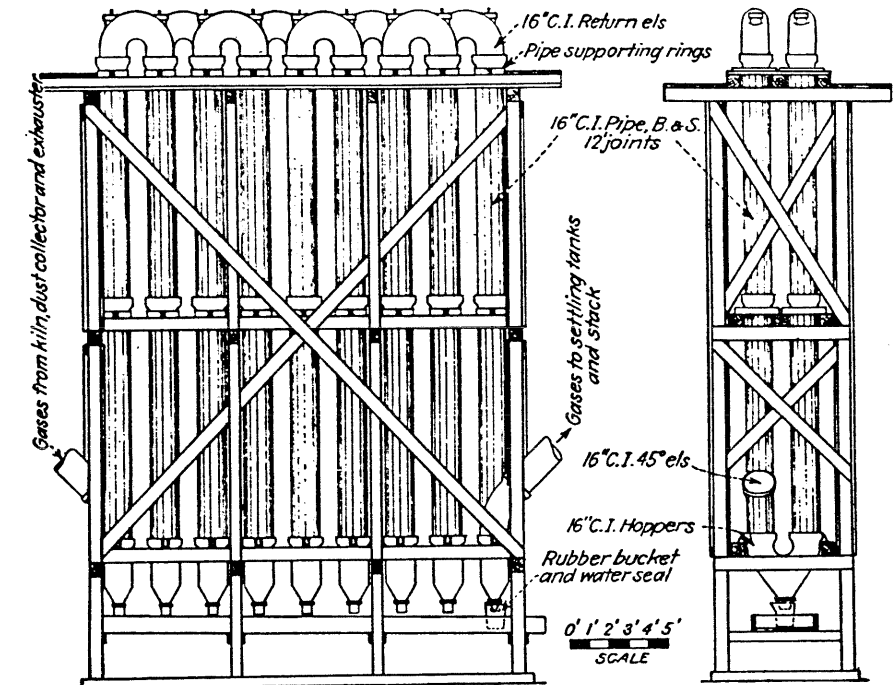


FIG. 8.—Single-row double-deck cast-iron condensing system.

zontal to vertical, by reversing the flow of the gas stream at frequent intervals. A number of different types have been illustrated in *U.S. Bureau of Mines Bulletins 222* and *335*[8]. The most popular European type of condensing system, known as the Cermak condenser, is made of stoneware and consists of pipe joints set vertically with return L's at the top and bottom, the bottom L's having an outlet to facilitate cleanup. The gas travels up and down through the system with frequent reversals of direction.

The tile systems used in this country were far better than the earlier brickwork designs, offering better cooling capacity, centralized cleanup, good baffling action, low cost, and as applied to the industry offered a generally better designed condenser than had been employed theretofore. Tile resists the corrosive action of the sulphurous acid condensed in the system and has a fair resistance to the thermal shock imposed by starting or stopping the operation of a plant or by a spray placed in the system

either for cooling or knocking down dust. In time, however, it has a tendency to crack and require repair.

Metal Condensers.—Although metal condensers had been tried on the brickwork furnaces, after the period of popularity of all-tile condensers (roughly 1917 to 1927), they were again introduced following tile-condenser design (except that pipes were always set vertically). Materials that have since been used, in the order of their popularity, are cast iron, sheet steel, stainless steel, and Monel metal. Each has been used alone, in combination with another, or in combination with tile pipes.

The use of metal pipes immediately draws the criticism of poor resistance to the corrosive effect of the acid condensate within the system. Cast-iron pipe is most commonly used and is probably included in more plants than any other material. One manufacturer uses exclusively a centrifugally cast iron pipe for which is claimed a much better resistance to corrosion than the ordinary cast iron. The pipe used is 16 in. in diameter, has a wall thickness of 0.45 in., and is made in 12-ft. lengths with bell-and-spigot ends. The systems are usually installed as shown in Fig. 8, in stands two lengths high and with specially cast return L's for making the top connection and specially cast hoppers for the bottom connection. In standardizing on a single size of pipe, the system may be sized in accordance with volume and velocity requirements, by length, and by splitting the gas stream into more than one row of pipes.

Although there is a definite relation between area or length or volume contained in the condensing system, it has been many times illustrated that the relation is not in direct ratio to the tonnage being treated. This is probably in part due to variations in excess air required in the different sizes of mechanical furnaces, differences in rate of heat transfer caused by different gas velocities, or differences in composition of furnace gases.

Table 3 shows the make-up of several sizes of cast-iron condensing systems applied to standard rotary furnaces with unit figures based on their maximum capacity in tons of ore treated per day.

The figures cited must be taken as average, as wide variations can exist owing to an extreme condition in one of the variable factors previously mentioned as affecting the design of a condensing system.

TABLE 3.—TYPICAL SIZES OF CAST-IRON CONDENSING SYSTEMS

Type ¹	Ton- nage	Pipes ²	Hop- pers ³	Re- turns ⁴	Total length, ft.	Ft. per ton capac- ity	Total area, sq. ft.	Sq. ft. per ton capac- ity	Rever- sals of direc- tion
SRDD	12	12	4	3	172	14.3	810	67.5	9
SRDD	25	16	5	4	228	9.1	1074	43.0	11
SRDD	40	28	8	7	396	9.9	1865	46.6	17
SRDD	60	32	9	8	452	7.5	2129	35.5	20
DRDD	100	40	12	10	568	5.7	2675	26.8	26
TRDD	150	60	18	15	852	5.7	4013	26.8	39

¹ SRDD indicates a single row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).

DRDD indicates a double row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).

TRDD indicates triple row of pipes, double decked (2- to 12-ft. joints, 24 ft. high).

² Pipes are cast iron, 16 in. i.d., 12 ft. long, 0.45 in. wall thickness, bell-and-spigot ends.

³ Hoppers are cast iron, 16 in. i.d., return L's, but with an outlet at the bottom for water seal and cleaning.

⁴ Returns are cast iron, 16 in. i.d., return L's, but with a cleanout hole over each outlet for cleaning of pipes.

In operation cast-iron condensing systems are simple and efficient. They operate at input temperatures varying from 450 to 250°F., and outlet temperatures of 100 to 160°F. Because a coating of quicksilver soot builds up on the walls of the pipes, they are periodically washed down at intervals ranging from 24 hr. to 14 days. The frequency depends on the amount of dust escaping the dust collector, the quantity of sulphur reprecipitated, the accumulation of soot or tars caused by imperfect combustion in the furnace, the amount of moisture and quicksilver in the ore, and occasionally on a routine requirement for shutdown for servicing power plant or other equipment. In multiple-row systems, dampers are occasionally installed so that one row may be washed down without necessitating a cessation of furnacing. The time required for washdown varies from about 30 min. to 2 hr. In the washing-down operation, a hose with a spray attachment is dropped into each stand of pipe through the cleanout holes in the returns. The soot, or mud, drops to the hoppers where it is caught in buckets under each hopper spout. The buckets are removed, emptied, and replaced for further operation. Between washdowns, there is a certain amount of "drop-down" which is collected daily or oftener if required. The ratio of material collected in the drop-down to that collected in the washdown varies considerably. In most instances the higher the sulphur content in the ore, the greater the hang-up, although on the average, the amount collected in the washdown approximately equals the total collected by daily drop-down. The buckets collect the drop-down continuously by maintaining a water seal over the hopper spout. The buckets used are usually hard rubber to resist the corrosive action of the water.

The cast-iron pipes, hoppers, and returns, though attacked by the sulphurous solutions, vary in life depending mostly on the sulphur content of the ore being treated. In the hot end of the condensing system and before the dewpoint of the water vapor is reached, they will last almost indefinitely. As the gas stream becomes wet, the metal is attacked, and in this portion of the system, the life varies from 1 to 5 years. Despite the requirement for replacement, but because of their low initial cost, the ease of installation, and their high rate of heat transfer, they are the most popular type in operation.

Sheet-steel condensers, of welded construction, designed to the same layout as the cast-iron system, have been installed in several reduction plants. They have been built of material ranging from 18 gage to ¼ in. thickness. Their resistance to corrosive attack is less than that of cast iron, and the lightweight material used only justifies their installation for the treatment of very low sulphur ores. They have been particularly popular in Nevada installations whose ores are most often of this type. Although they have a somewhat higher rate of heat transfer than cast-iron pipes, they are usually constructed in about the same sizes.

There were a few Monel-metal systems built, ranging in weight of material from 24 to 28 gauge; however, their performance did not justify the original cost.

Stainless steel, type 317, has been included in a combination system at Nevada property, together with sheet iron and cast iron. The system is made up of a large number of 9-in.-diameter pipes, 12-gauge black iron being used in the hot end of the system, cast iron being used in the middle, and stainless steel at the cold end. The resistance of the stainless to sulphurous attack is good; however, the occurrence of occasional chlorides in this ore adds a corrosive constituent to this gas not found elsewhere, and one that attacks the stainless-steel pipes.

Several installations have economically and efficiently combined sheet steel with cast iron and sheet steel with tile, in either case the sheet steel being installed on the hot end.

Several methods have been used for connecting the pipes at the top and the bottom of the stands; however, the most commonly used is a cast-iron or fabricated-steel

return L. Next in popularity is the use of tile Y branches, the straight section being set on a 45-deg. slope with the branch pointed vertically upward. Several Y branches may be joined to form a common base for several stands of pipe. The bottom end of the branch line is often submerged in a tank of water to provide a water seal and prevent leakage during cleanup.

The top connections are possibly more varied as to detail but usually simulate the return L, the Y branch, or a T, with or without cleanout openings.

It will be noted that in attempting to improve the cooling capacity of condensing systems, which ultimately resulted in largely swinging to metal condensers, the other objectionable features of earlier systems have also been improved. Costs, as shown later, are lower. The almost complete elimination of sprays, at least inside the system, has been advisable for several reasons: the satisfactory application of dust collectors has lessened their requirement for knocking down the dust; there is less water overflow from the condensers reducing water losses; the cooling efficiency of water in the system is poor; and the spray of water on a metal pipe hastens its failure by corrosion. Water sprays are sometimes applied to the outside of metal systems, although this is usually done to make effective an undersized system, to increase the capacity of a system, or to combat excessive summer atmospheric temperatures. Modern systems have been compacted so that cleanup can be made in a relatively small area and mechanical losses thereby reduced. The reduction in the health hazard has been one of the more important accomplishments of new systems. Leakage has been reduced to a minimum by making the condensers of an impervious material which upon the first break-through is easily detected and repaired; the method of cleanup exposes workmen to a minimum of quicksilver fumes; and, because of their simplicity and compactness, there is less quicksilver tied up to contaminate the atmosphere around a quicksilver plant.

Exhaust Fans.—Discussion of exhaust fans has been given ahead of description of the condensers as there are three locations—for either rotary or Herreshoff furnace installations—in which they have been placed.

The location determines the physical requirements necessary in the exhauster, although it is doubtful that there is any material metallurgical advantage in one location over another.

Many of the older brickwork plants used exhausters for maintaining a draft over the firebox, and these exhausters were nearly always located at the end of the condensing system or at the base of the stack. They operated in a wet and corrosive atmosphere at temperatures probably ranging from 90 to 140°F., and were commonly made all, or in part, of wood to resist corrosive attack.

In modern mechanical furnaces they have been placed (1) between the furnace and the dust collector, (2) between the dust collector and the condensers, and (3) between the condensers and the settling tanks or stack.

Although there were a number of installations made as in 1, the temperature of the gases at this point gave rise to operating difficulties in bearing wear and abrasive attack by the dust-laden gases. This was partly overcome by the use of water-cooled bearings, but these did not prove entirely satisfactory.

The bulk of installations are as in 2. At this point, gas temperatures are seldom over 400°F., and improvement in ball-bearing design and the inclusion of heat-reflecting plates and fans on the exhauster shaft make modern exhausters entirely satisfactory in this temperature range. By placing the exhauster after the dust collector, abrasive action of the dust is nearly eliminated and the gases are still hot enough to be dry and therefore noncorrosive.

The installation of the exhauster at the end of the condensing system has become more popular with the development of acid-resistant exhausters. The old wood-

scroll and wood-impeller designs are unsatisfactory; however, corrosion-resistant metals or rubber-coated exhausters are quite satisfactory. The latter are more commonly used and, barring accident to the coating, are useful for a long life.

It may be argued in favor of location 2 that (a) there is no corrosive attack by wet gases, (b) better dust-collector action and draft control is gained, and (c) any leakage in the condensers is immediately discernible and can be repaired. In favor of location 3, (a) severe bearing wear is eliminated, (b) a smaller volume of gases is handled because of the lower temperature, and (c) the condenser system is always under a negative pressure, thereby preventing leakage of fumes. There is probably little to choose by except individual preference and the somewhat higher cost of the rubber-coated fan.

All modern installations use electrically-driven exhausters, many of which are equipped with variable-speed drives in order to make adjustments easily and quickly to control draft properly under variable conditions. The power required varies from about 1 hp. at 10 tons daily capacity to 10 hp. at 150 tons per day.

Settling Tanks.—The utilization of settling tanks beyond the condensing system has become standard practice on most mechanical-furnace installations. Their function as a cooler in the condensing system is all but precluded by the fact that the gases at this point are wet and corrosive and that to be effective as a settling tank they must be large, so cannot be economically built of material with a high rate of heat transfer. As a consequence, they are commonly built of wood. Tanks have ranged from 5 to 24 ft. in diameter and 6 to 20 ft. in height, and may be installed singly or in number. In a commonly used tank, the staves are 20 ft. in length and the tank is 10 ft. in diameter and is supported by $\frac{5}{8}$ -in. steel-rod hoops. A conical redwood bottom facilitates cleanup. Entry, from the condensing system, is usually made by cutting a hole in the side of the tank, so that the entry pipe can be inserted on an upward angle anywhere above the cone. The exit pipe is similarly cut in just above the cone and may lead to another tank, or stack line, or the stack may be mounted on the side of the tank. Connection pipes are usually made of wood-stave pipe or tile.

Although these tanks are poor coolers, they do provide a settling area in which final traces of uncollected quicksilver may be collected. The reduction in velocity, plus the baffling effect gained by the eddying of the gas stream within the tank, assists in collecting the minute globules that may have carried through the condensing system attached to a particle of dust or droplet of water. In some installations, baffles or sprays have been added to the tanks.

The use of settling tanks adds a safety factor to the operation of all plants in standing by as additional collector in the event of misoperation of other units within the plant. Likewise, it provides a measure of over-all operation in that, if more than the usual amount of quicksilver is collected from the tanks, the condensing system, tonnage, and draft should be checked for changes from normal operational procedure. The normal amount collected, as in the condensing system, varies according to several factors; however, the tank system should not collect more than 1 per cent of the total quicksilver collected. If it exceeds this amount, stack losses may be excessive.

Stack Lines and Stack.—Beyond the tank system, the condensation and collection of quicksilver should have been essentially completed. The stack, therefore, is primarily to convey the gases of combustion, water vapor, sulphur dioxide, and other gases away from the plant for waste. The importance of a stack line, i.e., the line from the tank system to the base of the stack, has largely declined with the universal application of exhaust fans to provide draft control. There are some, however, who continue to advocate their use, although it would seem that their only advantage

would be as an additional collecting facility or to raise the stack to such an elevation that power requirements on the exhaust fan are reduced. Modern plants are, therefore, about equally divided between those using a stack line and those which mount a stack on or alongside the final tank. Stack lines, likewise, are about equally divided between tile and wood construction, whereas stacks are almost entirely of wooden construction. Redwood is the commonly used wood in the construction of tanks, connection pipes, and stacks, although fir has been used. It withstands the action of the acid quite well, and the life of these units will probably average 5 to 10 years. The temperature of the gas at the stack should not exceed 140°F., lest high stack losses be encouraged. They will run down to relatively low temperatures depending upon the atmospheric temperature.

Soot Machines.—Soot machines have been developed to handle the product of the condensing system, commonly referred to as "soot" or "mud," although in most of the older plants, and even up to quite recently, it was worked by hand. Soot includes dust that escaped the dust collector and was knocked down in the condensers, unoxidized sulphur precipitated out of the gas stream, residues from unburned fuel, precipitates from other volatile constituents of the ore (As, Sb, etc.), water and quicksilver. It is collected in buckets or launders under the condensers, settling tanks, and from the stack line and stack. The quantity varies greatly, as previously shown, as does the percentage of the constituents.

Older practice consisted of decanting the water from soot, mixing in unslaked lime to dry it and make the finely divided (floured) quicksilver coalesce into large globules, and hoeing. The soot was placed on an iron table varying in size from 12 to 50 sq. ft. with 4-in. sides and set with a slope to one corner. It was then manually hoed (mixed and raked) across the table, and the separated quicksilver flowed to the low corner, from which it overflowed through a gooseneck to a storage pot.

Under the table, steam or hot-water pipes and not uncommonly a wood fire assisted in drying the soot and facilitated the separation. The quicksilver fumes escaping from the table, though probably not so large as to constitute a serious loss of quicksilver, contaminate the surrounding atmosphere with a concentration sufficiently high to be dangerous to the workmen. Various ventilating systems have proved only partially successful.

Because of this hazard, the cost of labor, and the fact that a sometimes rather low recovery is made by hand-hoeing, numerous mechanical devices have been devised.

The most widely used is a circular pan, 3 to 6 ft. in diameter, with a vertical central shaft to carry mixing and stirring paddles. The soot and lime are placed in the pan and hoed by the rotation of the paddles either for a predetermined period or until the soot is impoverished of the bulk of the quicksilver. For best operation, the paddles rotate at 5 to 10 r.p.m., and the pan is set on an inclination of about 1½ in. per ft. A slot at the low point of the pan, connected with a gooseneck, creates a puddle which assists in the collection of the finely divided quicksilver. The pan may or may not be equipped with a heating device, although a hot-water compartment, kept at 150 to 160°F., materially improves results. The top of the machine may be tightly enclosed, thereby preventing fume leakage. When driven through a worm reducer, the power required ranges from 1 to 5 hp.

Many other devices have been used, some with good success, but the above type is most commonly used. Other types include agitators (both wet and dry), centrifuge types, presses, screw classifiers, and probably many others.

In most instances the hoed soot is returned to the furnace feed so that the unreclaimed quicksilver in the soot is ultimately recovered. At some plants a retort is kept in operation for the treatment of the hoed soot on the basis that returning the soot to the furnace only increases the dust problem. Because the soot collected

seldom exceeds 10 per cent of the dust collected, this does not seem important, and at several operations tests showed that dust conditions were no less favorable when the dust was returned to the furnace.

Auxiliary Equipment.—Additional equipment required in the modern furnace plant is not extensive and includes that common in other milling plants, such as bins, crusher, screens, conveying or elevating equipment, and a power plant.

Bins required are for coarse and fine ore and for burnt ore. Many of the new plants have utilized steel bins for fine ore and burnt ore but have kept wood bins for coarse-ore storage. The result is larger coarse-ore storage and a reduction in fire hazard in the main plant. Many concrete burnt-ore bins are in use, and although they have a tendency to crack from the heat, their usually small size (10 to 75 tons capacity) does not make this serious.

The crushing of quicksilver ores is perhaps less difficult than that of many others. Except for the opalite and rhyolite ores of Nevada and Oregon, a few hard limestone ores, and still fewer hard serpentine ores, most quicksilver occurs in sandstones or shales that are relatively easy to crush. In preparation for rotary furnaces, the ore does not have to be reduced to less than 2 to 3 in., which can be accomplished in a single pass through a jaw crusher. Inasmuch as hearth furnaces require a smaller size of feed, installations for plants of this type usually include a jaw crusher in closed circuit with a shaking screen and necessary conveyer or elevators. Because the greatest number of quicksilver plants fall within the range of 20 to 75 tons daily capacity, jaw crushers commonly range from 6 × 8 in. to 10 × 20 in. in size and are mostly of the Universal or Blake type. Screens, where used, are of the shaker type and are sized according to the hearth-furnace requirements.

Conveyers or bucket elevators, because of the usually small capacity required and because plants are relatively compact, are not extensive.

TABLE 4.—INSTALLED HORSEPOWER REQUIREMENTS FOR ROTARY-FURNACE PLANT INSTALLATIONS

	Daily plant capacity, tons					
	8-12	12-25	25-40	40-60	60-100	100-150
1. Kiln.....	1	2	3	3	5	7½
2. Feeder.....	1	2	3	3	5	7½
3. Exhaust fan.....	1	2	3	5	7½	10
4. Compressor for oil firing.....	3	5	7½	10	15	25
5. Oil pump.....	¼	¼	½	½	¾	1
6. Oil preheater.....	¾	1¼	2	2½	3¼	4
7. Crusher.....	5	7½	10	15	20	25
8. Conveyer.....	1	2	3	3	5	7½
9. Lights and miscellaneous.....	2	2	3	3	5	10
10. Total horsepower installed.....	15	24	35	45	66½	97½
11. Usually installed generator, kw.	15	20	30	40	50	75

Items 4, 6, 7, 8, and 9 are at average conditions.

The power requirements for all quicksilver-reduction plants are relatively small. Although the number of plants that are served by power companies are increasing, the majority of plants have to generate their own. The power consumed in the early plants, as already stated, was little and was usually steam. This was replaced with

the development of the oil engine, and up to the First World War most plants were line-shaft driven. Since that time, however, the improvement of diesel engines has been responsible for their greater application together with alternating-current generators. This has made possible individual electric drives on each piece of equipment with attendant greater flexibility and efficiency.

The installed horsepower requirements of rotary-furnace installations, together with the usually installed size of diesel-generator plant, are shown in Table 4. Requirements for compressor and oil preheater are subject to change for altitude and climate conditions; for the crusher depending on type of ore; and for conveyer and lights and miscellaneous, on topographic, camp, layout, and other factors.

Actual power consumption will be approximately one-half the installed horsepower when the plant is operating continuously.

Control of Operations and Assaying.—Quicksilver-plant operators largely depend on the manufacturer to provide a furnace designed to operate efficiently within a certain tonnage range on a particular type of ore. As a consequence, it is up to the manufacturer, based on an estimation of the various factors previously described, and experience, to provide a plant meeting the tonnage specifications. Tangible and intangible factors are, therefore, considered in such design, and after installation is made certain tests can be performed to set up operating conditions at various tonnages. Likewise, such tests should be performed when changes of ore occur, as in character, grade, and moisture and sulphur content, or when equipment or other related conditions are changed.

The tests consist of making an accurate determination of the weight of the ore being treated and its moisture content; the grade of ore must be determined; the fuel consumption must be measured; a determination of the CO₂ content in the furnace gases must be made; and pressure and temperature readings must be taken throughout the plant. With the results of these tests in hand and as described in more detail in *U.S. Bureau of Mines Bulletin 335*[8], it is possible to adopt operating conditions within safe limits.

In practice it is common to measure ore by occasionally weighing a cubic foot and then assigning weights to cars, trucks, or other means employed to transport the ore into or away from the plant. Few plants weigh automatically or continuously. Likewise, occasional checks are made on moisture content and grade of ore. The difficulty in sampling of quicksilver ores due to the erratic occurrence of the cinnabar in the ore and its friability and tendency to concentrate in the fines increases the difficulty of checking metallurgical operation; however, if carried out carefully and with due recognition of the factors involved, sampling will give good results. Assaying the samples is usually performed in the Whitton apparatus or by the so-called Bureau of Mines method[9], the latter being preferred because of its greater accuracy and because assays may be made more quickly.

In the Whitton method, the ore sample, together with fluxes, is placed in a metal retort tube closed at one end. A clean, weighed gold or silver foil is placed over the open end and a metal cup clamped down on it, sealing the retort. The cup is filled with water, and as the retort is heated, the quicksilver vapor rises in the retort to the foil, on which it condenses and amalgamates. The foil is again weighed, the increase showing the amount of quicksilver in the sample.

The Bureau of Mines method, described in detail in *Technical Paper 227*, consists of volatilizing the quicksilver in a sample, in a test tube, and collecting the quicksilver on the cold upper walls of the same test tube. After complete volatilization of the quicksilver, the lower half of the test tube, including the burnt sample, is broken off and discarded. The upper half including the condensed quicksilver is washed with nitric acid in a beaker, potassium permanganate added to this solution until it

remains colored, and peroxide added until the color disappears. With ferric sulphate as an indicator, the solution is then titrated with potassium thiocyanate. This method is simple and can easily be used in plant control work for checking head samples and also burnt-ore samples.

Fuel consumption is measured either by meter or by gauging fuel tanks and for the purpose of test periods can be measured quite accurately.

Determination of the CO₂ content of the furnace gases should be made in order to determine the total gas volume and the amount of excess air drawn through the furnace. From the former it is possible to calculate stack losses, and from the latter a measure of the thermal efficiency of the plant is gained. These determinations need not be made at frequent intervals after operating conditions are established.

The use of a draft gauge to measure pressures throughout the system and a thermometer to check temperatures at frequent intervals are the two most practical applications to control of operations. If it is assumed that, after a general checking of one plant, operating conditions have been established within certain ranges, the draft gauge and the thermometer give a relative indication of all conditions. As a consequence, these are the only instruments generally relied on for indicating or recording, continuously, conditions affecting control. Thermometers are usually installed to measure temperature of the gas stream somewhere between the furnace and the condensers, and occasionally at the end of the condensers and at the stack. Draft gauges are usually installed on the furnace at the gas outlet and occasionally in the condensers or at the stack. A manometer is often installed at the fan to measure the back pressure of the dust collector. The usefulness of draft gauges is their ability to measure changes in pressure in the system caused by leakage or by plugging so that proper steps may be taken to alleviate the trouble.

For the most part, quicksilver plants operate with very little control apparatus after they have once been adjusted and regulated. Occasional check tests are very desirable, but normal operation is usually left to the operator, who, by observation, can quite easily detect changes in conditions as they develop. Because simple regulation to offset these changes is possible, automatic control devices are not usually justified.

Losses.—Losses in quicksilver-reduction plants may occur at the following points: (1) in the burnt ore, (2) in the dust, (3) through the stack, (4) by solution or mechanically in water overflow, (5) by spillage and through handling.

Losses in the burnt ore are primarily a function of the temperature at which the rock is burned and the period it remains at or near that temperature. In most operations the burnt-ore loss can be considered as very small, although on low-grade ores the economy of striving for complete extraction is sometimes offset by fuel cost versus increased furnace capacity and greater gross production. It is difficult to establish the point at which one offsets the other, owing to the differences in burning characteristics of different types of ore, cost of fuel oil, and the price obtained for the quicksilver produced. In properly operated furnaces, however, and on average grade ores, the burned rock may show average assays of 0.02 to 0.05 lb. per ton. Many operations checked show lower values than these, and of course, there are some that run higher.

Dust losses have been discussed and the amount shown to be, on average ores (ores averaging less than 8 lb. per ton), approximately equal in grade to the grade of the ore. If the dust collected represents $\frac{1}{4}$ of 1 per cent to $2\frac{1}{2}$ per cent of the ore feed, these figures would represent the loss in the dust if no attempt was made to recover any of the values from it.

Stack losses have probably been blamed in more instances than anything else for the failure of a plant to recover quicksilver from the ore; however, most operators as well

of rotary-furnace-plant operations based on 1944 and 1941 conditions. Actually, costs for the period 1935-1939 would approximate 20 to 30 per cent lower than the 1941 figures.

TABLE 6.—ESTIMATED COST OF OPERATION OF ROTARY-FURNACE PLANTS, 1941 AND 1944

	Average of daily rated capacity, tons per 24 hr.					
	10	18½	32½	50	80	125
Firemen, number required.....	3	3	3	3	3	3
Cleanup men, number required.....			1	1	1	2
Foremen, number required.....					1	1
Labor cost per ton, 1944.....	2.85	1.54	1.17	0.76	0.63	0.48
Labor cost per ton, 1941.....	1.80	0.92	0.74	0.48	0.43	0.32
Oil consumption, gallons per ton.....	7½	7	6½	6	5½	5
Oil cost, per ton.....	0.64	0.60	0.42	0.39	0.36	0.33
Supplies, repairs, power and maintenance, per ton.....	0.60	0.50	0.40	0.35	0.30	0.20
Total operating cost, per ton, 1944.....	4.09	2.64	1.99	1.50	1.29	1.10
Total operating cost, per ton, 1941.....	3.04	2.02	1.56	1.22	1.09	0.85

Although these figures are based on hypothetical requirements, they approximate actual costs for the two periods mentioned. Labor costs for firemen and cleanup men are based on \$9.50 per day, average daily wage (7 days per week, including 1 day at time and one-half and 1 day at double time), including compensation insurance, social security, and unemployment insurance, for 1944, and \$6 per day for 1941. Foremen are bracketed at \$12 per day in 1944 and \$10 per day in 1941, being the average daily rates over a monthly period.

The variation in oil consumption is purely hypothetical, although it may be stated as average figures. A difference of 2 cents per gallon is allowed on the cost of fuel oil for the two smaller sized plants, their fuel being figured at an average of 8½ cents per gallon, whereas the larger kilns are assumed to use heavy oil at 6½ cents per gallon.

Supplies, repairs, power, and maintenance are estimated, in a liberal amount, to cover these items. Supplies include only lime for hoeing. Repairs and maintenance are generous enough to provide, over a period of 2 or 3 years' operation, for all charges. Power is figured at an average for purchased or locally generated power, including repairs to power plant if locally generated.

While these figures are estimated as average figures for rotary-furnace operations, there may be substitutal variations in either direction depending on ore characteristics and local conditions, although they may be used for estimating purposes. The sometimes lower quoted costs of Scott or other brickwork-furnace operations, and even other rotary- or hearth-furnace operations, if translated to present conditions, variations in ore being treated, or other operational factors, would approximate the figures of Table 6.

Description of Plants. New Idria Mine, California.—Figure 9 shows the flow sheet of the New Idria plant. Furnace equipment consists of four 5 × 6 ft. rotaries built in 1917. They have recently been rebuilt and the complete plant modernized. The burnt-ore bins are concrete. The kilns are fired with 16 to 18° Bé. fuel oil in National Aerol burners. Air pressure is 90 lb. per sq. in. and oil pressure 28 lb. per

sq. in. The firing hoods are so designed as to mix the air and oil in a mixing chamber and fire through a combustion block, all set outside the kiln, in order to gain as great an effective length in the kilns as possible. Shaker feeders feed an average of 100 tons per day to kilns 1 and 2, and 120 tons per day to kilns 3 and 4. Gases are drawn from each kiln by American Blower Co. No. 35 exhausters through No. 12 Sirocco dust collectors. The condensing systems on kilns 1 and 2 include forty 16 in. × 12 ft. cast-iron pipes with 12 hoppers and 10 returns; on kilns 3 and 4 each system includes 60 pipes of the same size and 18 hoppers and 15 returns. Numbers 1 and 2 are double-row double-deck systems, and Nos. 3 and 4 are triple-row double-deck systems. The

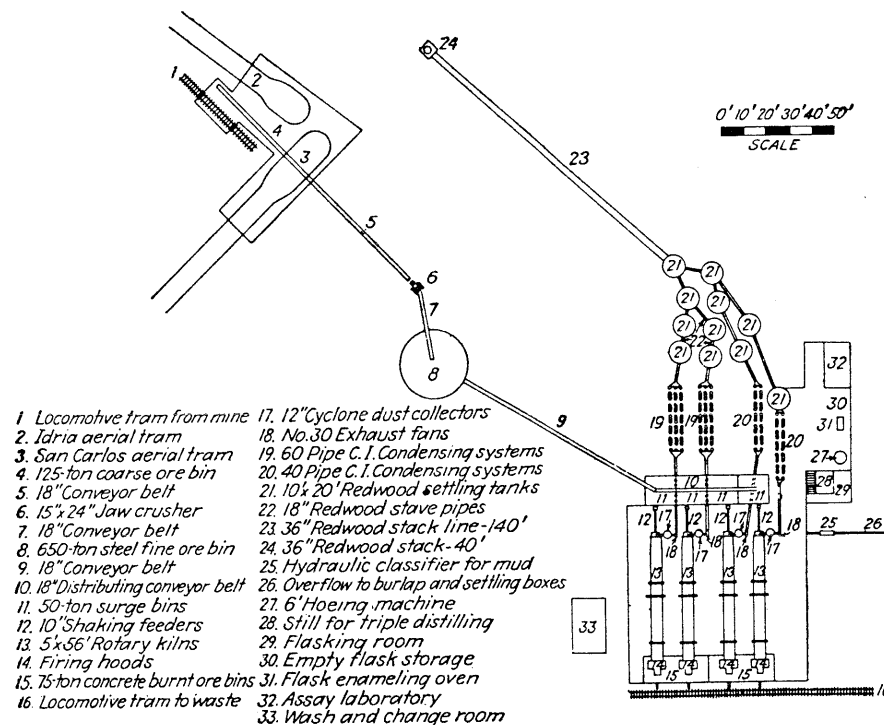


FIG. 9.—New Idria flow sheet.

tank system, as illustrated, is made up of 10-ft. diameter by 20 ft. high redwood tanks with 2-in. staves. The stack line consists of a 36-in. redwood continuous pipe to a concrete stack base supporting a 36-in. redwood stack 40 ft. high. It will be noted that each kiln and condensing system is kept separate until the middle of the tank system is reached. Dust is removed continuously from the collectors hydraulically and is combined with all condenser-system overflow water and all spillage on the floor and run through a specially designed hydraulic classifier. All soot is mechanically hoed and the soot returned to the furnaces. The quicksilver, after leaving the soot machine, is washed and flows directly into storage tanks, from which it is drawn for flasking. All flasking is done through a volumetric weighing device to ensure accurate measure. Ore is transported from the mine by two aerial tramways and by electric haulage to a tramway terminal bin of 125 tons capacity. From this bin it is conveyed to a 15 × 24 in. jaw crusher, all being reduced to minus 3 in. A second con-

the Reed is a 4 × 60 ft. rotary. In the original installation at the Sulphur Bank and in an earlier installation at the Reed, the furnaces were arranged for counterflow operation. Experience showed, however, that the free sulphur and the petroleum burned in the upper or drying end of the kiln but burned incompletely, owing to lack of oxygen, thus causing the precipitation of sulphur and petroleum soot in the condensing system.

This situation was so troublesome that the kilns were rearranged for parallel flow in order that the ore, upon being fed to the kiln, is immediately exposed to the highest heat and most oxygen, thus more completely burning off the sulphur and petroleum. Although in this type of kiln, the lower end is used for soaking, advantage cannot be taken of the drying effect in the upper portion of a counterflow kiln, and fuel consump-

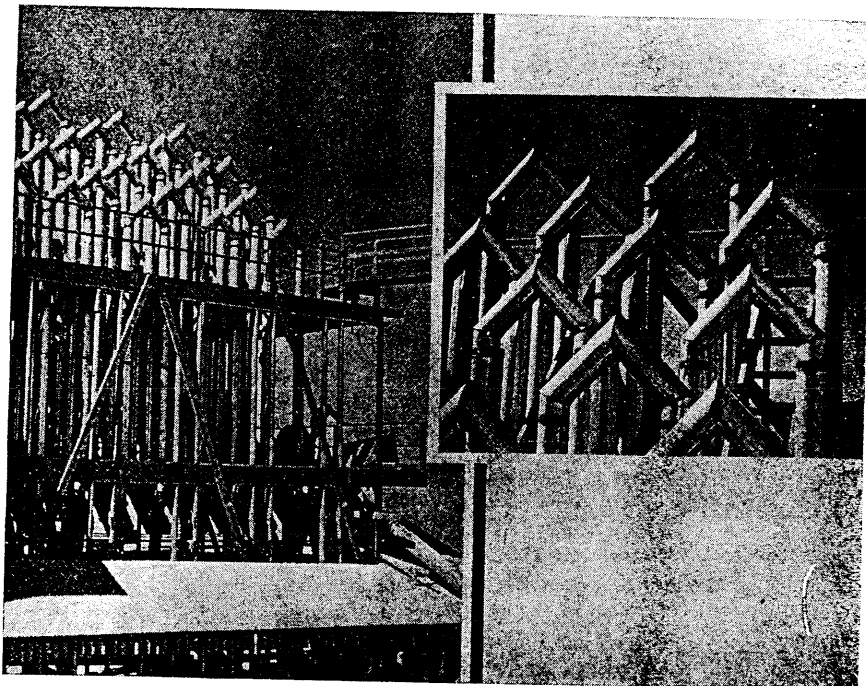


Fig. 11.—Cordero mine condensing system.

tion and temperature of gases leaving the kiln are both considerably higher. Fuel consumption in these operations ranges between 15 and 20 gal. per ton, and exit temperatures approximate 1000°F. This latter fact requires (or permits) that considerable cooling be accomplished before the gases reach the condensing system. "In the case of the Reed plant, longer than usual pipe runs between the kiln and cyclone type of collector and between the collector and a cast-iron condensing system act as the cooler so that gases enter the cast-iron system at near normal temperatures."

This is a special problem known only at these mines, and there have been no other successful parallel-flow rotary-kiln installations.

Red Devil Mine, Alaska.—The furnace at this mine is a 3 × 40 ft. rotary furnace of 20 to 25 tons daily capacity with 8-in. shaker feeder, 10-in. Sirocco dust collector, No. 25 American Blower Co. exhaust fan, cast-iron condensing system made up of 16 in. diameter pipes, two 10 ft. diameter by 20 ft. high redwood settling tanks, 110 ft.

of 18-in. redwood stackline, and a 40 ft. high 18 in. diameter redwood stack. The furnace is fired with wood fuel, and consumption amounts to approximately 11 to 12 tons per cord of wood. Good combustion is obtained and, possibly because of the character of the wood used, no wood tars are condensed in the condensing system. Ore is hand-trammed and hoisted from the mine into a 20-ton coarse-ore bin which feeds an 8 × 15 in. jaw crusher. It is crushed to minus 2 in. and fed to a conveyer belt that elevates and feeds a 40-ton steel fine-ore bin directly over the furnace feeder. The capacity of this furnace is somewhat reduced by comparison with other installations of the same size for the following reasons: because of wood firing, the volume of the gases of combustion is considerably greater than for oil firing; the ore carries an average of 1 to 3 per cent arsenic and 5 to 10 per cent antimony, either of which may at times exceed twice these amounts, and thus requires a greater volume of air for oxidizing these volatile components; and the moisture content of the ore is relatively high (10 to 20 per cent). Because the cinnabar is intimately associated with the arsenic and the antimony, it is necessary to make a nearly complete elimination of these metals in order to effect a complete recovery of the quicksilver. Unless sufficient air is provided to oxidize the stibnite, it has a tendency to melt, thus causing the ore in the kiln to stick to the brickwork. Careful control of fire and draft, however, makes it possible to get a good elimination of all quicksilver from the ore without clinkering in the kiln. Because of the relatively large amounts of antimony and arsenic in the ore, and because it was found necessary nearly to eliminate it from the ore by roasting, a large bulk of the oxide of the two metals was collected in the condensing system. This bulky precipitate was a part of the soot and made recovery of the quicksilver from the soot considerably more difficult than is normally the case. By hand hoeing it was found that frequently less than 10 per cent of the quicksilver could be recovered so that two D retorts, which had been used in prospecting the mine, were put into use to burn the soot after hoeing. This provided a good recovery, however, and the procedure was adopted. Despite the large amounts of antimony and arsenic present, the contamination of the quicksilver by either of these elements was practically nil. Sampling of 1000 flasks showed no arsenic and 0.003 per cent antimony.

Hermes Mine, Idaho.—The reduction plant consists of two modern rotary furnaces, 4 × 64 ft., having a capacity of approximately 140 to 150 tons per day. With dry ore in the summer, this capacity is somewhat exceeded; however, during the spring thaw the ore is very wet and the tonnage may be 15 to 25 tons less than this. The kilns are oil fired with heavy oil (16 to 18° Bé.), and fuel consumption varies with the moisture content. The collectors are No. 11 Siroccos and are followed by American Blower Co. No. 30 exhaust fans. Condensing systems include forty 16 in. diameter by 12 ft. lengths of cast-iron pipe with 12 hoppers and 10 returns, set up as a double-row double-deck system. Two 10 ft. diameter by 20 ft. high redwood settling tanks with conical bottoms, in series, follow the cast-iron system. Redwood stack lines and stack follow the tanks. In order to lower the temperature and knock down any quicksilver in the settling tanks, several grids made up of 1 × 2 in. fir, with 2 in. square openings, were placed one over the other in the tanks. A spray of water introduced at the top of the tank made each tank a washing tower, and although little quicksilver is collected, it is reported to have justified the installation. Firing is effected through high-pressure oil burners, each kiln being equipped with a 15-hp. compressor for atomization. All dust collected in the collectors, amounting to about 500 lb. per day per kiln and being of too low value to warrant re-treatment, is sluiced away from the plant with water. The high-grade soot collected in buckets under the condensers is normally hoed on a water-heated hoeing table. The residue from this operation, plus other low-grade soot, is dried in a tunnel drier extending through the burnt-ore bin and returned to the fine-ore bin.

Concentration of Quicksilver Ores.—The general opinion, by most quicksilver operators and others who have investigated the possibilities, that concentration of quicksilver ores cannot compete with direct furnacing, has largely been borne out by the failure of this method to remain or to become firmly established. Like the development of furnacing and condensing equipment, most experimenting and most installations were made when the price of quicksilver was high and operators more prosperous. Consequently, it is reasonable to believe that better than average engineering was applied in the attempted development of concentration methods. Likewise, there was the counterpart of the "get by as cheaply as possible" retort builder whose concentration plant was not destined to efficient operation. There have been, therefore, several periods in which development advanced more rapidly than in others.

Although wet crushing and treatment of ores is known to have been carried on in Italian mines as early as the seventeenth century, little is known of the methods or results obtained. The first known American concentration plant was at the San Carlos mine (now a part of the New Idria mine) where riffle boxes and rockers were used in 1871. Other similar operations are reported from a number of localities until, in the period from 1910 to 1916, many mills were built.

Most of the mills built during this period were gravity-concentration plants. They employed many types of mills including Huntington, Chilean, ball, rod, or roll; some plants used no mills or depended upon screens or trommels to sort out coarse material. Classifiers were not always used, thus giving a mixed feed to the concentrator with resultant less efficient performance. Concentrators included several types of tables, Frue vanners, and occasionally jigs.

In a few plants, flotation cells were added in an attempt to recover values ordinarily lost in the slimes, and a few all-flotation plants were installed.

The results of the mills operated during this period were similar in that they all showed poor recovery. In the straight gravity-concentration plants, the friability of cinnabar and the actual or attendant overgrinding of the ore caused large slime losses. The frequent failure to size the feed to the tables closely meant less efficient operation of the tables, and additional losses were incurred. The employment of flotation to recover slime losses was handicapped by the infancy of the flotation process at that time, the cost of fine grinding, and, in one case, by the exorbitancy of royalties demanded for the use of the flotation cell. Because of the variety of flow sheets used and differences in ore treated, it is difficult to estimate average recoveries made; however, they probably ranged from 25 to 85 per cent, with the better designed and larger mills approximating 60 to 70 per cent. Operating costs ranged from \$0.50 to \$1.25 per ton. When it is considered that roasting of the concentrates, either in retorts or by combining with furnace feed, and the cost and loss incurred in this operation is an addition to the milling costs, the comparison with direct furnacing is definitely in favor of the latter.

An excellent description of milling operations in this period is given by Bradley[11].

The advances made in flotation were in part responsible for increased interest in milling plants from 1927 to 1931. During this period, several flotation plants were built. The plant built at the Sulphur Bank mine in California was designed to overcome the problem of large amounts of free sulphur in the ore, an objectionable feature in furnacing. Despite several years of experimentation and operation, however, the mill was abandoned and direct furnacing reemployed.

During this same period and in the few years following, a number of gravity-concentration plants were built including the use of jigs of the Bendelari, Pan-American, and Southwestern types. The development of these jigs, with large capacity and efficient recovery and their successful use on gold dredges and in many metal mills,

led to their application in several quicksilver-recovery plants. They were usually combined with trommels or shaking screens and riffle boxes, without any mills. Several of these plants were installed to treat old mine dumps or burnt-ore dumps. Recoveries obtained were of the same order as in previous concentration plants; however, their low initial and operating costs made them economically profitable operations.

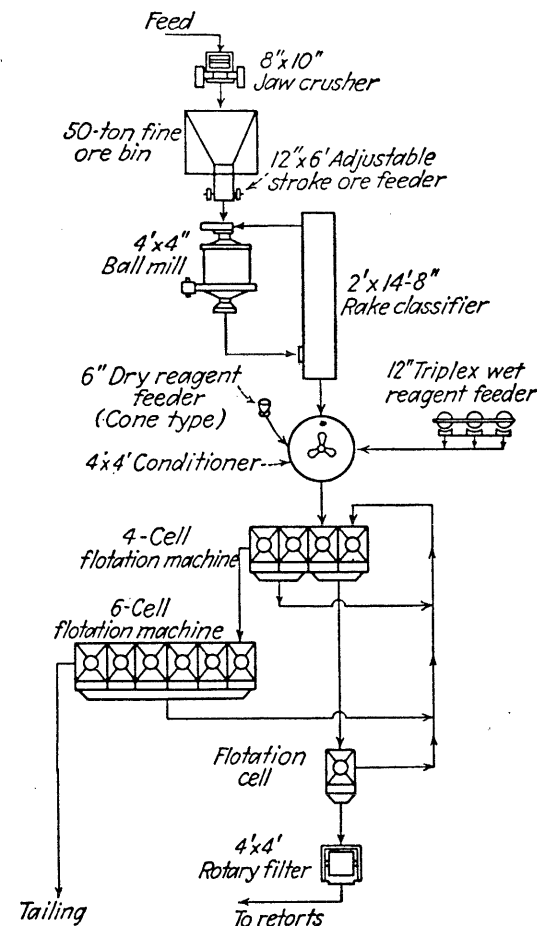


FIG. 12.—Beneficiadora de Mercurio, S.A., flow sheet.

In 1940, the Denver Equipment Co.[12] installed a modern flotation mill on the properties of Compañía Mercurio en Sain Alto and Beneficiadora de Mercurio, S.A., in Zacatecas, Mexico. The flow sheet of this mill is shown in Fig. 12. The ore occurs in sandstones and shales, cinnabar being the predominant sulphide with lesser amounts of metacinnabarite, pyrite, and arsenopyrite. Some graphitic and carbonaceous material also occurs in the ore.

A partial analysis of a sample of the ore showed: Hg, 0.55 per cent; As, 0.10; Fe, 4.30; insoluble, 74.60; S, 9.57.

The plant has a capacity of 60 tons per 24 hr. The ore is crushed to minus $\frac{1}{2}$ in. and ground to minus 65 mesh at 67 per cent solids. The ball mill is in closed circuit

with the classifier, which overflows to the conditioner. Conditioning time is approximately three minutes, and all reagents are added to the conditioner in order to suppress the carbonaceous and gray slimes. Reagents used per ton are Yarmor F pine oil, 70 g.; potassium ethyl xanthate Z-3, 30; Reagent 105, 20; starch or Reagent No. 637, varies depending on free carbon content. Dilution of the circuit is held to 4:1, and a pH of 7.2 is maintained for best flotation results. Discharge from the filter carries approximately 15 per cent moisture and is retorted. Mill data over a representative period, Nov. 15 to Dec. 5, 1941, is shown in Table 7.

TABLE 7.—MILL DATA, BENEFICIADORA DE MERCURIO, SAIN ALTO, ZACATECAS, MEXICO

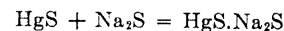
Product	Weight, %	Tons per 16 hr.	Hg, %	Recovery %
Heads.....	100.00	33.33	0.67	100.0
Concentrates.....	1.39	0.46	46.21	95.4
Tailing.....	98.61	32.87	0.03	4.6

The metallurgical results of this operation are interesting and show that modern flotation practice, possibly together with an especially amenable ore, can produce results approaching direct furnacing. If costs can be held sufficiently low to offset a sometimes greater loss, there is a definite place for flotation in the metallurgy of quicksilver ores.

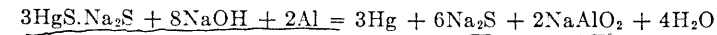
Generally speaking, however, experience has shown that gravity concentration, at best, cannot approach direct furnacing, owing in part to slime losses and also to the inability of the concentrators to make a high recovery. Higher recovery can more easily be made at the sacrifice of grade of concentrate, a fact that has made economically profitable the operation of concentration plants in mines where furnaces are installed and operating. Very low-grade ores can be raised sufficiently to make them of furnace grade at relatively low cost and good recovery, as was done at the New Idria mine. Old mine dumps and burnt-ore dumps in 1938-1941 were mined by power shovel, trucked to a bin, passed over a grizzly set at 2 in. and a shaker screen with 5/8-in. openings. All coarse material was hand-sorted for high grade and the minus 5/8-in. then passed over a 42-in. Benedlari jig and thence to about 100 ft. of riffle boxes. The grade of product collected was 6 to 10 lb. per ton from 1 to 2 lb. per ton in the material as mined. Recovery was 40 to 60 per cent, but costs were low enough to justify the operation.

Flotation of quicksilver ores has been handicapped by the nonuniformity of most quicksilver ores and the cost of fine grinding. There is quite possibly a place for flotation if all factors are properly considered in advance. Unfortunately, large deposits of quicksilver ore, justifying a large milling plant with its low initial and operating unit costs, which are uniform, and moderately easy grinding, are not yet known.

Chemical Treatment of Ores.—The only wet chemical treatment process for the reduction of quicksilver which has received considerable attention depends on the solubility of metallic quicksilver or cinnabar in a solution of sodium sulphide and sodium hydroxide, although other alkaline sulphides may be used. The caustic hydroxide is necessary only in small amounts to secure the maximum solvent power of the sodium sulphide over the cinnabar. The reaction is represented by the equation



and the recovery of the quicksilver from the solution is made by precipitation with aluminum according to the equation



Although the electrolytic deposition of the quicksilver from the alkaline sulphide solution has been considered, the precipitation by aluminum seems to have an advantage due to the regeneration of the Na_2S .

Thornhill[13] has described the recovery of quicksilver from amalgamation tailings using this process in an operation at the Buffalo mines, Cobalt, Ontario, during 1915. This is the only commercial-scale operation of this type known, and although results were reported as satisfactory, it was not applied to cinnabar ore.

Various experiments have shown as many results; however, it is not generally believed that, because of chemical-consuming constituents of many ores, the cost of fine grinding, irregularity as to composition of ore feed (so common in many quicksilver mines), difficulties in filtering, cost of aluminum, and over-all recovery, the process can compete with modern furnace treatment of quicksilver ores.

Mercurial Poisoning.—Inasmuch as all persons exposed to quicksilver are subject, in greater or lesser degree, to mercurial poisoning, or salivation, as it is usually called around the mines and reduction plants, certain precautions and fundamentals of design or operation should be considered.

The principal symptoms of chronic mercurial poisoning, usually developing in this order until all three are evident, are stomatitis, psychic irritability, and tremors. Davenport and Harrington[14] report in considerable detail each of these symptoms and further point out the variation in sensitivity of different people to mercurial poisoning. Continued exposure to an atmosphere contaminated with quicksilver vapor is recognized as being more harmful than intermittent exposure inasmuch as elimination of quicksilver entering the body through the respiratory passages, the gastrointestinal tract, or through the skin is slower than absorption.

Figures on what is considered to be a dangerous contamination, likewise, vary over a great range depending on the sensitivity of the individual and whether or not he has previously been exposed. The figures range from 0.1 mg. per cu. m. of air up to 10 or 20 mg. per cu. m.; however, the California Industrial Hygiene Service and the Industrial Accident Commission of California have adopted a limit of 0.15 mg. per cu. m. of air[15].

Precautions to be taken to prevent mercurial poisoning are listed[14] and generally include personal cleanliness and good housekeeping around the reduction plant. In design and operation of the various types of plants, leakage of fumes or dust should be prevented, good ventilation provided in all dangerous areas, protective clothing and respirators worn by workmen when subject to exposure, and mechanical soot-treating devices used to the greatest extent in order to reduce exposure.

The fact that attention has been devoted to this subject with successful results is evidenced in the compensation insurance rates for workmen in this classification in California, where three mines pay between \$2.98 and \$3.86 per \$100 of pay roll, depending on the experience rating of the mine. This compares with surface-mining rates of \$3.50 to \$4.50 and underground-mining rates of \$7 to \$9 per \$100 of pay roll.

BIBLIOGRAPHY

1. AGRICOLA, GEORGIUS: "De re metallica," translated by H. C. and L. H. Hoover, London, 1912.
2. BECKER, GEORGE F.: Geology of the Quicksilver Deposits of the Pacific Slope, U.S. Geol. Survey Monograph, Vol. 13, 1888.

3. DUSCHAK, L. H., and C. N. SCHUETTE: The Metallurgy of Quicksilver, *U. S. Bur. Mines Bull.* 222, 1925.
4. GOULD, H. W., and Co., San Francisco, Calif.
5. Pacific Foundry Co., San Francisco, Calif.
6. WILLISTON, S. H.: Mining Quicksilver in Nevada, *Mining Congr. Jour.*, November, 1942.
7. DUSCHAK, L. H., and C. N. SCHUETTE: Fume and Other Losses in Condensing Quicksilver from Furnace Gases, *U.S. Bur. Mines Tech. Paper* 96, 1919.
8. SCHUETTE, C. N.: Quicksilver, *U.S. Bur. Mines Bull.* 335, 1931.
9. BOUTON, C. M., and L. H. DUSCHAK: The Determination of Mercury, *U.S. Bur. Mines Tech. Paper* 227, 1920.
10. EGGLESTON, T.: Treatment of Mercury in Northern California, *Trans. A.I.M.M.E.*, Vol. 3, 1876.
11. BRADLEY, WALTER W.: Quicksilver Resources of California, *Calif. State Mining Bur. Bull.* 78, 1918.
12. Denver Equipment Co., Compañía Mercurio en Sain Alto and Beneficiadora de Mercurio, S. A., *Bull.* M4-B24, July, 1942.
13. THORNHILL, E. B.: Recovery of Mercury from Amalgamation Tailing, *A.I.M.M.E. Bull.* 104, 1915.
14. DAVENPORT, S. J., and D. HARRINGTON: Mercury Poisoning as a Mining Hazard, *U. S. Bur. Mines Circ.* 7180, November, 1941.
15. RANDALL, MERLE, and H. B. HUMPHREY: New Process for Controlling Mercury Vapor, *U. S. Bur. Mines Circ.* 7206, April, 1942.
16. DENNIS, W. H., *Mine & Quarry Eng.*, Vol. 8, pp. 277-280, 1943.

CHAPTER XVII

CHLORINE METALLURGICAL PROCESSES

BY DONALD M. LIDDELL *Reinvestigate*

Chlorine as a metallurgical reagent appears to have lost ground during recent years, and much of what follows is of historical rather than operating interest. However, it is a question in the author's mind whether the great decrease in price of chlorine and the large sources of supply that will be available after the war do not warrant reinvestigation of the applicability of chlorine processes to present-day metallurgy.

EARLY HISTORY

Chlorine has been used almost exclusively for the recovery of gold and silver. It has been used to some extent in the treatment of low-grade copper ores, but never in a major metallurgical process for the recovery of copper. The use of chlorine in the metallurgy of other base metals has been subsidiary.

High-grade gold and silver ores and high-grade base-metal ores containing small or large amounts of gold and silver are usually smelted to recover the metals. Chlorine has been associated only with hydrometallurgical processes (including amalgamation), usually for low-grade ores, but sometimes for high-grade siliceous ores remote from other facilities for treatment.

The earliest hydrometallurgical process for treating gold and silver ores was amalgamation. The date when mercury was first used for this purpose is unknown. Amalgamation of gold was known to the Romans and was recorded by Pliny, but no reference is made to silver. For the oxidized ores near the surface—where the gold and silver were in metallic condition or the silver occurred as a haloid—this process was simple, but when deeper mining reached sulphide ores another method had to be devised to put these metals into a condition to be amalgamated.

The first recorded use of mercury in the metallurgy of silver, and in connection with it the first recorded use of chlorine in any metallurgical process, occurs in a treatise entitled "De la Pirotechnia," by Vanoccio Biringuccio, published in Venice in 1540.² In this treatise it is stated that the ore (previously roasted, if refractory) was finely ground in a stone mortar, screened wet, and dried. The dry ore was moistened with vinegar or water, in which had been dissolved mercuric chloride, copper sulphate, common salt, and sometimes ferrous sulphate. The ore pulp was then covered with mercury and ground, or stirred, in the mortar for an hour or two. The tailings were washed away with water, and the silver was recovered by retorting the amalgam.

The Patio process for the treatment of silver ores, involving the same chemical reactions as those in the process just described, was invented by Bartolomé Medina, a miner of Pachuca, Mexico, in 1557.³ The invention of this process is credited to

¹ This chapter is a major revision of the chapter contributed by the late Stuart Croasdale to the first edition of the handbook.

² Percy, "Metallurgy of Silver and Gold," pp. 559-562. London, 1880.

³ *Op. cit.*, p. 561.

losses by volatilization, von Patera introduced steam into the furnace during the chloridizing roasting. This process was first introduced in America by Ottokar Hofmann, in 1868, at La Dura, Sonora, Mexico; it was gradually adopted at other mines in Mexico and the United States, reaching the zenith of its application during the succeeding 25 years, until the demonetization of silver by the government of the United States in 1893 closed every leaching plant in this country that had been treating silver ores.

Up to this time, and for a number of years afterward, gold in ores that had been subjected to a chloridizing roast was supposed to be converted into the chloride, which decomposed into chlorine and metallic gold at a temperature below 300°C. Hence, if gold occurred in silver ores, it was converted into metallic gold by chloridizing roasting and was not recovered by any of the solvents used for the extraction of silver.

Plattner Process.—Plattner proposed converting the gold into chloride by means of chlorine gas and extracting it with water. This process was introduced in Silesia, Germany, in 1851. The ore was either roasted "dead" or, if it contained silver, it was chloridized by roasting with salt. The silver was first leached out by brine or "hypo-sulphite" solution, then chlorine gas was applied to the ore in the vats. The gold was recovered by subsequent leaching with water and precipitating by means of ferrous sulphate (see Wet Chlorine-gas Processes).

Longmaid-Henderson Process for Copper Ores.—The treatment of copper ores by chloridizing roasting was first patented by Longmaid in 1844 and was first applied to the extraction of copper from pyritic residues or calcines by William Henderson of Scotland in 1859–1860.¹

Pyrites from Spain and Norway, which were used throughout Europe for making sulphuric acid, contained 3 to 8 per cent of copper. After the pyrites were roasted for the manufacture of sulphuric acid, the residues were again roasted with salt by the Henderson process, to convert the copper into chloride. The chloridized ore was then leached with water or dilute acid, and the copper was precipitated from the solution by iron.

The gases from chloridizing roasting contained sulphurous acid, hydrochloric acid, and chlorine. To prevent these gases from becoming noxious to the neighborhood, and to utilize their acids, they were passed through coke towers sprayed with water, which collected not only the acids but any volatilized metallic chlorides as well. The water from the scrubbing towers was used for leaching the chloridized ore.

This process was patented in the United States in 1866 and was in constant use, both in this country and Europe, for over 60 years. It will be further described under the paragraph on copper ores in the section on Chloridizing Roasting and Leaching Processes.

When the residues or ores contained silver, that metal was precipitated from solution as an iodide by the *Claudet process* before the precipitation of the copper.

Hunt & Douglas Process.—About the same time, 1862, ferrous chloride was suggested by Schaffner and Unger, of Germany, as a solvent for copper in ores. This method was developed later in the United States into the Hunt & Douglas process. It was designed to treat oxidized copper ores with siliceous gangue.

Ferrous chloride was made by dissolving copperas (ferrous sulphate) and common salt in water. An excess of salt was then added, and the sulphate of soda was removed as much as possible by crystallization. This solution, therefore, became a brine solvent containing a soluble base-metal (ferrous) chloride. The process was appli-

¹ EISSLER, MANUEL, "The Hydrometallurgy of Copper, being an account of processes adopted in the hydrometallurgical treatment of cupriferous ores, including the manufacture of copper vitriol, with chapters on the sources of supply of copper and the roasting of copper ores," pp. 87–104, London and New York, 1902.

cable to raw ore containing oxide or carbonate of copper and was later applied to the separation of silver and copper in roasted matte, because silver minerals are likewise soluble in the brine as prepared. The copper was precipitated on scrap iron in the usual manner. If silver was present, it was first removed by precipitation on copper.

The Hunt & Douglas process passed through many modifications on account of the difficulty of treating ores containing any carbonate of lime or magnesia, both of which precipitate the iron from the solvent. It was abandoned many years ago and was replaced by smelting and electrolytic refining. Acid leaching has replaced it in hydrometallurgy.

The Doetsch process,¹ using ferric chloride as a solvent for copper, was invented about this same period to treat the sulphide ores at Rio Tinto. An attempt was made in 1914 to revive this process under the name of the *Slater process*,² but it did not pass the experimental stage. The feature of the Slater process was the regeneration of the ferric chloride. A lixiviant containing ferric chloride and hypochlorous acid was produced by suspending ferric hydroxide in the anode compartment of a cell in which a salt solution was electrolyzed. After the dissolution of the copper from the ore, ferric hydroxide was precipitated from the lixivium by means of the sodium hydroxide produced in the cathode compartment of the electrolytic cell. Under the highly oxidizing conditions in the solution, ferric hydroxide can be preferentially precipitated in this manner without precipitating any of the copper. The ferric hydroxide precipitate was returned to the circuit in the anode compartment for the generation of new lixiviant, and the copper was recovered from solution by the usual methods. The only reagent required was common salt. The process was not adapted to basic ores. A slight modification of this process was developed by the Midland Ores & Patents Co.³ at Waverly, N. J., in which the solution containing ferrous chloride, after precipitating the copper on iron, was regenerated direct by electrolysis, yielding ferric chloride for new lixiviant and metallic iron for copper precipitation (see page 540).

The Hoepfner process for copper ores⁴ was introduced in Germany in 1891. The copper ore was leached in revolving barrels with a solution of cupric chloride and salt or calcium chloride. The lixivium was purified by precipitating the silver on metallic copper, by cooling to separate the lead chloride, by adding powdered limestone to precipitate the arsenic, antimony, and bismuth, and by the use of air in a special manner to precipitate the iron as oxide. It was then electrolyzed to precipitate part of the copper as pure metal, and to regenerate cupric chloride for leaching new ore. Owing to difficulties in manipulation, the process was not a commercial success.

Hoepfner Process for Zinc Ores.⁵—The ore was roasted with salt at a temperature not to exceed 650°C. and leached with hot water. The solution was purified by cooling to 5°C. to crystallize out the sodium sulphate, by adding bleaching powder and marble dust to precipitate the iron and manganese, and by adding powdered zinc to precipitate the other electronegative metals. The purified zinc and sodium chloride solution was electrolyzed for the production of metallic zinc and the recovery

¹ CUMENGE, Notes sur le Rio Tinto, *Ann. mines*, Vol. 96.

² MORSE, H. W., The Slater Leaching Process for Copper Ores, *Mining Sci. Press*, Jan. 24, 1914, p. 181.

³ Leaching at Yerrington, *Mining Sci. Press*, July 17, 1915, p. 94; PERRY, R. W., Leaching Oxidized Copper Ores with Ferric Chloride, *Mining Sci. Press*, May 17, 1919, pp. 669–674; MIDDLETON, PERCY R., Ferric Salts as Solvents in the Leaching of Roasted Copper Ores, *Eng. Mining Jour. Press*, Sept. 9, 1922, pp. 452–453.

⁴ *Z. angew. Chem.*, 1891, p. 160; *Offizielle Zeitung der internationalen elektrotechnischen Ausstellung*, Frankfurt am Main, No. 27; EILERS, KARL, Hoepfner's Electrolytic Copper Process, *Eng. Mining Jour.*, Apr. 30, 1892, p. 471.

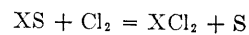
⁵ GUENTHER, E., Electrolytic Zinc Extraction by the Hoepfner Process, *Eng. Mining Jour.*, May 16, 1903, pp. 750–752; *Mineral Ind.*, Vol. 6, pp. 668 and 675; Vol. 7, p. 743; and Vol. 9, p. 688.

of chlorine to make bleaching powder. The process was used for a short time in Europe.

transferred to trans. for met.

Swinburne-Ashcroft Process for Complex Ores.—The use of chlorine gas in the metallurgy of lead, zinc, and other base metals was brought into commercial prominence by Swinburne and Ashcroft of England, who obtained their first patents in 1897.¹ In the original process, as operated at Broken Hill, Australia, dry chlorine gas was applied under pressure to the dry and coarsely pulverized sulphide ore in a closed shaft furnace known as the "transformer." The chemical reactions involved are strongly exothermic and supplied all the heat necessary for operation. By regulating the flow of chlorine gas to the supply of fresh sulphide ore, a temperature of 600 to 700°C. could easily be maintained in the transformer.

The reaction between dry chlorine gas and a mineral sulphide results in the formation of a metallic chloride and free sulphur, as shown by the equation



Fe & Mn

At the temperature named, the sulphur distilled from the top of the transformer and the fused metallic chlorides, with the gangue in suspension, were tapped from the bottom. The metals were recovered by substitution; the fused chlorides, as they came from the transformer, were stirred into a bath of molten lead, which decomposed the precious metal chlorides and recovered these metals in the form of a high-grade lead bullion; from the lead bath the fused chlorides were drawn to another kettle and treated with zinc to recover the lead; the remaining chlorides were then dissolved in water and treated with chlorine gas to oxidize the iron and manganese; zinc oxide, obtained by roasting high-grade blende, was added to this solution to precipitate the iron and manganese as oxides, which were removed, along with the gangue of the ore, by filtration. As will be seen by following this line of substitution, all the original chlorine was ultimately combined with zinc, and the filtrate from the iron and manganese oxides was a commercially pure solution of zinc chloride. In the final phase of this process, the zinc-chloride solution was evaporated to dryness and the zinc chloride fused and electrolyzed for the recovery of metallic zinc and the regeneration of the chlorine gas.

The process was cyclic. There was no appreciable loss of chlorine at any stage of the operations, and all the substitution metals were produced by the process itself, but the process did not prove successful as designed and operated. Its operation was limited to sulphide ores or concentrates carrying not over 30 per cent gangue, in order to maintain the temperature required.

A modification of this process was developed by *Baker and Burwell*, of Cleveland, Ohio, in 1904-1908.² The finely pulverized dry ore was placed in a porcelain-lined tube mill provided with lead-lined trunnions, and supplied with flint pebbles. Low-grade complex ores were treated, and in the absence of a high percentage of sulphur the temperature was kept down to 100°C. Dry chlorine gas was admitted to the tube mill, and chemical action began at once. As the tube mill revolved, the pebbles ground off the metallic chlorides as fast as formed and constantly exposed fresh

¹ SWINBURNE, JAMES, Chlorine Smelting, with Electrolysis, *Trans. Faraday Soc.*, July 1, 1903; *Mining Sci. Press*, Aug. 8 and 15, 1903; *Electrochem. Ind.* (now *Chem. Met. Eng.*), Vol. 1, pp. 412-413, August, 1903; Vol. 2, p. 404, October, 1904; Vol. 3, pp. 63-66, February, 1905; *Eng. Mining Jour.*, Aug. 1, 1903; STEINHART, O. J., "Chlorine Smelting," *Mining Sci. Press*, Nov. 28, 1903; ASHCROFT, E. A., *Trans. Inst. Mining Met. (London)*, June 19, 1901; *Mineral Ind.*, Vol. 9, pp. 692-693; Vol. 10, pp. 267 and 677-682.

² BAKER, CHARLES E., A New Application of Chlorine in Metallurgy, *Trans. Am. Electrochem. Soc.*, Vol. 12, pp. 115-163, October, 1907; *Electrochem. Met. Ind.* (now *Chem. Met. Eng.*), Vol. 5, p. 448, 1907; Vol. 6, p. 433, 1908; BAKER and BURWELL, Electrolytic Chlorination Process, *Mining Sci. Press*, Feb. 4 and 20, 1905.

surfaces of ore to the action of the chlorine; they also broke up any lumps that might be formed. The free sulphur that was formed remained with the ore. If the temperature was allowed to get too high, considerable sulphur chloride was formed, which distilled off at about 150°C.

After chlorination was completed, the ore was discharged from the tube mill and leached with water, thus giving a clean solution of metallic chlorides free from sulphur and gangue. The metals were recovered from the aqueous solution by substitution. The gold and silver were precipitated on copper, the copper on lead, and the lead on zinc. After oxidation with chlorine gas, the iron and the manganese were precipitated by means of zinc oxide, and the zinc and the chlorine were recovered by the electrolysis of the fused chloride as in the Swinburne-Ashcroft process. A couple of experimental plants were erected in Montana in the years that followed, but, owing to operating difficulties, they did not prove successful. The most serious difficulties were to evaporate zinc chloride solution without the formation of basic salts and the consequent loss of chlorine as hydrochloric acid, and also the development of a satisfactory cell for the electrolysis of the fused zinc chloride.

About this time, John L. Malm, of Denver, Colo., began experimenting with the Baker-Burwell process, which he greatly modified and developed. This will be described as the *Malm process*¹ in the section on Dry Chlorine-gas Processes.

Pohlé-Croasdale Volatilization Process.—Loss of metals from volatilization during chloridizing roasting was known already when Plattner undertook a study of the conditions and extent of this loss in an elaborate series of experiments on both oxidizing and chloridizing roasting. The results of his experiments were published in his "Metallurgische Rostprozesse" (1856). He mentioned considerable loss of silver chloride when it came in contact with other easily volatilized chlorides and discussed at length the volatile products of the chloridizing roasting, but he failed to record any loss of gold by volatilization.

Loss of gold by volatilization was recognized from time to time² and was the source of serious monetary loss in treating gold-silver ores by chloridizing roasting, but the cause of this loss seemed to be little understood. It was generally attributed to tellurium,³ and not to chlorine, because the chlorides of gold were supposed to decompose into the constituent elements at a temperature below 300°C.; therefore, all gold should remain in the ore in metallic condition. The first person to recognize chlorine as the source of this trouble was C. H. Aaron,⁴ but after many experiments on roasting California gold ores with salt he came to the conclusion "that gold is volatilized in some form not easily condensable."

Christy⁵ investigated this subject in the best chlorination mills in California as well as in the laboratory during the early eighties, and came to the conclusion that losses of both gold and silver increase (1) with increased percentage of salt added during the roast; (2) with increase of time and temperature during roasting; and (3) when salt is added after a long oxidizing roast instead of at the start. Christy qualifies the last statement by saying that, "while there is a rapid volatilization of gold and silver when

¹ TRAPHAGEN, F. W., Dry Chlorination of Sulphide Ores, *Mining Sci. Press*, April 10, 1909, p. 522; HERRICK, R. L., The Malm Dry Chlorination Process, *Mines and Minerals*, January, 1910, p. 370; IONIDES, S. A., Dry Chlorination of Complex Ores, *Mining Sci. Press*, May 27, 1916, pp. 781-787; MAIER, C. G., Possibilities of Dry Chlorination of Oxidized Zinc Materials, *Eng. Mining Jour.-Press*, Vol. 115, pp. 51-54, January, 1923.

² CHRISTY, S. B., The Losses in Roasting Gold Ores and the Volatility of Gold, *Trans. A.I.M.E.*, Vol. 17, p. 8, 1888-1889; DEBRAY, H., Note sur le chlorure d'or, *Compt. rend.*, Vol. 69, p. 984, 1869.

³ KÜSTEL, GUIDO, Roasting of Gold and Silver Ores and the Extraction of Their Respective Metals without Quicksilver, p. 57, San Francisco, 1880; CHRISTY, *op. cit.*, p. 3.

⁴ AARON, C. H., "Leaching Gold and Silver Ores, the Plattner and Kiss Process, a Practical Treatise," p. 121, San Francisco, 1881.

⁵ CHRISTY, *op. cit.*, pp. 3-44.

salt is added at the end of the roast, the gold chloride is quickly decomposed by the SO₂ gases and by the raw ore itself in the cooler end of the furnace, and the gold is redeposited in metallic form, so that the actual loss is not so great as when salt is added at the beginning of the roast."

Stetefeldt¹ expressed his opinion that the gold escaped as a double salt, and, if this were true, the loss of gold depended on the volatility of the chloride with which the gold chloride was combined.

In an earlier treatise,² Aaron states that the base metals are chloridized by chloridizing roasting, but they are not volatilized to any extent, while Küstel³ takes the opposite view and states that "base metals as sulphates take up their share of salt and consume a large portion, but, as their chlorides are volatile, the salt is a means of getting rid of a great deal of the metals during roasting which are not desirable in the ore for subsequent treatment of silver."

The foregoing constitutes a brief summation of the knowledge of volatilization up to 1898. Much that is recorded is contradictory. There was no thought of making a commercial extraction by volatilization, and the recovery of the volatilized chlorides, if attempted, was only a phase of the general treatment of the ores.

In 1891-1893 Croasdale discovered that a commercially complete (above 90 per cent) volatilization of gold could be obtained from Cripple Creek ores by roasting with salt. About the same time, Pohlé independently obtained similar results with silver ores from Aspen, Colo. Systematic investigation of the volatilization of metals as chlorides was begun by these men in 1898 and was carried on with a large-scale experimental plant until 1903.⁴ Numerous investigators⁵ have worked on this process since that time. The process will be further discussed in the section on Chloride Volatilization Processes.

CHLORIDIZING PROCESSES FOR RAW ORES

With the exception of the Malm process, chlorine processes for raw ores of the precious metals are necessarily confined to the treatment of surface ores, or to clean gold and silver sulphide ores in which the gold and silver sulphide minerals are not combined with base-metal sulphide minerals. To obtain a commercial recovery of

¹ STETEFELDT, C. A., The Amalgamation of Gold Ores, and the Loss of Gold in Chloridizing Roasting, with Especial Reference to Roasting in a Stetefeldt Furnace, *Trans. A.I.M.E.*, Vol. 14, pp. 336-351, 1886.

² AARON, C. H., "A Practical Treatise on Testing and Working Silver Ores," San Francisco, 1876, pp. 35-36.

³ KÜSTEL, *op. cit.*, p. 29.

⁴ CROASDALE, STUART, Volatilization of Metals on Chlorides, *Eng. Mining Jour.*, Aug. 29, 1903, pp. 312-314; Sept. 19, 1903, p. 420; *Mining Mag.*, London, March 1914, pp. 200-204; MATHER, HENRY A., *Eng. Mining Jour.*, Sept. 5, 1903, and Oct. 17, 1903, p. 576; HAWKINS, EDWIN N., *Eng. Mining Jour.*, Oct. 3, 1903, p. 490; ROSE, SIR T. K., "Metallurgy of Gold," p. 291, London, 1915.

⁵ VARLEY, THOMAS, and others, *U. S. Bur. Mines Bull.* 211, 1923; the chloride volatilization process of ore treatment, being a complete compilation of the work that has been done on this process; LAYING, HARAI R., Chloridizing Processes, *Mining Sci. Press*, Jan. 17, 1920, pp. 77-83; Chloride Volatilization Process, *Mining Sci. Press*, Aug. 27, 1921, p. 284; Thermal Requirements of Chloridizing Volatilization, *Mining Sci. Press*, Feb. 25, 1922, pp. 264-266; Chloridizing Volatilization—Some Experiments and Their Practical Application, *Eng. Mining Jour.*, Nov. 12, 1921, pp. 764-770; BRADFORD, ROBERT H., The Volatilization Process at the Pope-Shenon Mine, *Mining Sci. Press*, Aug. 20, 1921, pp. 263-266; VARLEY, THOMAS, and C. C. STEVENSON, Development of the Chloride Volatilization Process by the U. S. Bureau of Mines, *Eng. Mining Jour.*, June 11, 1921, pp. 991-993; VARLEY, THOMAS, Chloride Volatilization, *Eng. Mining Jour.*, Feb. 18, 1922, pp. 276-278; GAHL, RUDOLF, Heat Requirements in Chloridizing Volatilization, *Eng. Mining Jour.-Press*, June 3, 1922, pp. 957-958; RALSTON, OLIVER C., Heat Requirements of Chloridizing Volatilization, *Eng. Mining Jour.-Press*, Apr. 15, 1922, pp. 614-615; HOWE, BEN, Gold Recovery by Volatilization, *Monthly Jour.*, *West Australian Chamber of Mines*, December, 1912; *Mining Mag.*, London, March, 1913; *Mining Sci. Press*, Mar. 29, 1913, p. 484; Oct. 4, 1913, p. 535.

the gold and silver, the base metal sulphide minerals should not exceed 2 or 3 per cent; if more than this amount, concentration or roasting should precede the chloridizing process. Ores in which the silver is combined with arsenic and antimony as sulphides must be treated by chloridizing roasting to liberate the silver, or leached with alkaline sulphides. Base ores containing carbonates of lime and magnesia are not adapted to these processes, owing to their precipitating action on the metallic chlorides, which prevents reaction on the silver minerals. The gradual disuse of these processes has been brought about by the world-wide depletion of surface or suitable ores and the necessity of other methods of treatment for the complex sulphide ores that come with deeper mining; also by the possibility of treating lower grade ores on a larger scale at less cost by the cyanide process. Base-metal recoveries are made with the Malm process.

The **Patio process** is still used in isolated districts of Mexico and South America, but with modern machinery and methods of transportation it has been almost completely replaced by the cyanide process and by the custom-smelting plant. A complete description of this process is given on page 517. Therefore, a brief outline of its relationship to chlorine metallurgy will suffice here.

The salt and copper sulphate react to form sodium sulphate and cupric chloride. Some cuprous chloride is formed by the action of mercury on cupric chloride, and this is dissolved by the brine in the ore pulp. Both cupric and cuprous chlorides react on the sulphides of silver, forming silver chloride and copper sulphide. The silver chloride is dissolved by the brine in the torta, and the silver is precipitated in metallic form by the mercury, after which it is immediately amalgamated. Mercuric and mercurous chlorides are formed by the chemical reactions. Considerable silver sulphide is said to be reduced directly to metallic silver by the mercury, with the formation of mercuric sulphide.

The recovery of silver by this process will range from 75 to 80 per cent on favorable ores, but will drop below 60 per cent on ores containing an appreciable amount of base-metal sulphides, particularly blende or arsenical and antimonial sulphide minerals.

There is a chemical loss of mercury in the form of soluble chlorides, as well as a mechanical loss due to the flouing of the mercury by surface chemical action of sulphide minerals, but the total loss is not so much as would be expected. It is said to amount to about one and one-half times the silver recovered.

This process is applicable only where labor and the few necessary supplies are cheap, equipment and freight are costly, and time of little importance. For example, the Noche Buena and Feliz Ano mines in the Totolapam district, about 75 miles east of Oaxaca City, Mex., in 1925 had in active operation six patios and were preparing to build six more. Extraction by the patio process was reported by the manager to be unusually high. Excessive freight rates, by muleback transportation, on stamp-mill concentrates caused the mine owners to enlarge their patio facilities.¹ The writer has not been able to obtain recent information.

The **pan-amalgamation process** was evolved from the "cazo" or caldron process. In Europe, where it was first used, the amalgamating was done in revolving barrels and was known as the "barrel-amalgamation" process. Pan amalgamation seems to have been an American development, and it was first operated in the United States at Washoe, Nev., in 1861. For a long time it was known as the "Washoe process."

The "pan" was made wholly of cast iron, or with a cast-iron bottom and wooden sides. In either case the bottom was made hollow for the introduction of steam to heat the charge. Cast-iron mullers for grinding, stirring, and amalgamating the

¹ *Eng. Min. Jour.-Press* (Sept. 5, 1925), 386.