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(54) MANUFACTURE OF SODIUM CHLORATE

(57) **Abstract:**

This invention relates to the manufacture of alkali metal chlorates by an improved electrolytic process. In particular it relates to the use of an air-cathode for the manufacture of alkali metal chlorate, notably sodium chlorate.

Electrolysis of alkali metal brine is well-known as a method for the production of alkali metal hydroxide and chlorine. Such electrolysis is carried out in cells having separate cathode and anode compartments to minimize reaction of chlorine with alkali metal hydroxide which results in product loss. In chlorate manufacture by electrolysis it is not desirable to keep the anolyte and catholyte separate. In fact contact of the liberated chlorine with electrolyte is necessary to form hypochlorite and chlorate. These reactions may be expressed by the equations:

$$2\ Cl^- \longrightarrow Cl_2 + 2e$$

$$Cl_2 + 2\ OH^- \longrightarrow ClO^- + H_2O$$

$$Cl_2 + H_2O \longrightarrow HClO + Cl^- + H^+$$

$$2\ HClO + ClO \longrightarrow ClO_3^- + 2\ Cl^- + 2\ H^+$$

The last reaction is favored by high temperature and requires no electric current to result in chlorate formation. Operation of commercial cells is carried out in an acid environment to favor formation of HClO and avoid the anode reaction which is promoted by high pH as follows:

$$6\ ClO^- + 3\ H_2O \longrightarrow 2\ ClO_3 + 1.5\ O_2 + 4\ Cl^- + 6\ H^+ + 6_e$$

This latter reaction occurs in anolyte at pH values greater than 7 and leads to a maximum current efficiency of 66 per cent whereas the former reactions approach a theoretical current efficiency of 100 per cent. Yield reduction and loss in current efficiency are due to cathode reduction of the hypochlorite and chlorate ion. A small amount of sodium dichromate is generally added to the cell brine feed to prevent reduction of hypochlorite and chlorate ions at the cathode.

Generally, graphite anodes and steel cathodes are employed to result in a potential drop across the cell of 3.5 to 3.7 volts.

Now it has been discovered that air-cathodes can be prepared which are particularly useful for providing low voltage drop across chlorate cells. Thus, large power savings may be realized as a result of lower cell voltage. Further, it has been discovered that these chlorate cells with such cathodes may be and preferably are operated without dichromate. Hence, improved efficiency may be obtained while simultaneously avoiding contamination resulting from the addition of dichromate. These and other advantages will be apparent from the detailed embodiments disclosed herein.

In accordance with this invention a method has been developed for the production of alkali metal chlorates, notably sodium chlorate which comprises electrolyzing brine containing a substantial concentration of alkali metal chloride, notably sodium chloride, at a pH of 5 to 9, preferably 6 to 7, while oxygen-bearing gas is provided at electrolyte-electrode interface. Thus, electrolysis is typically conducted in a cell the cathode of which is made of electrically conducting oxygen-activating catalyst on chemically inert porous substrate having an interface provided with adventitious pores through which oxygen may be supplied from an oxygen-bearing atmosphere contained within the electrode interior. A positive pressure within the electrode interior is provided to cause the appearance of oxygen-bearing gas at the electrolyte-electrode interface.

Electrodes for use as air-cathodes in the present invention are fabricated from porous material to permit application of a gas pressure to the interior of the electrode. Suitable gas pressure is just sufficient to cause the appearance of oxygen-bearing gas at the electrolyte-electrode interface and is generally 0.01 to 0.5 atmospheres above the external pressure. Material for fabrication of the cathode is typified by porous carbon. Such porous carbon may be drilled to provide a hollow interior and may also be machined to provide means of attachment for fittings by which the oxygen-bearing internal atmosphere, such as air or oxygen gas may be supplied. Such a porous carbon support may be converted into a useful electrode by a variety of procedures. By way of illustration a porous carbon electrode supplied with an internal atmosphere of air may be specially electroplated with oxygen-activating metallic catalysts, notably platinum. Platinum is deposited in the pores of the porous carbon from a platinum chloride solution containing 10 grams per liter of platinum at a current density of 40 milliamperes per square centimeter. While the platinum coating is being deposited the internal atmospheric pressure is alternately raised and lowered to keep the pores of the porous carbon from becoming completely blocked or plated over and to result in deposition of oxygen-activating platinum within the pores. Similar procedures may be employed to apply other platinum group metals which serve as oxygen-activating catalysts. The platinum group metals are: rhodium, ruthenium, palladium, osmium, iridium, and platinum.

Other air-cathodes, comprising a noble metal on which is deposited a film of a transition metal oxide, are prepared by plating noble metal on the porous support, followed by a treatment to deposit a thin film of selected metal oxide thereon. Deposition of the metal oxide may be accomplished by electrolysis of a solution containing a halide of the metal selected, by way of illustration, chromic chloride. Alternatively, a low concentration of metal halide, such as chromic chloride, may be added to brine of an alkali metal, such as sodium chloride, from which the film of metal oxide is deposited by electroplating on the cathode.

A type of air-cathode may also be prepared by soaking porous carbon cathodes in an aqueous solution of a salt such as chromium nitrate from which active chromium oxide cathodes result by simply heating to 250°C. These cathodes may be made especially active by depositing a platinum group metal, such as platinum, thereon.

Porous supports other than carbon may be employed when the air-cathode contains an oxygen-activating substance such as a spinel. In this embodiment a cathode having a hollow interior is fashioned from porous metal such as nickel or iron, by sintering the powdered metal at a temperature sufficiently high to cause the metal particles to adhere to each other without actually melting. Alternatively, a hollow porous cathode of the metal may be fabricated from a fine screen of the metal wire. Such metal support is then dipped in a solution containing soluble salts of an appropriate metal, such as aluminum nitrate mixed with chromium nitrate in aqueous solution. The treated electrode is then ignited and heated to a temperature approximately 1200°C. to result in formation of mixed metal oxides having the characteristic crystalline structure of spinels. Similar results may be obtained by application of an oxide paste or aqueous slurry prior to ignition.

It is necessary that cathodesfor use in this invention be prepared from porous substances which are electrical conductors. However, porous cathodes may be fabricated by sintering non-conducting coarsely ground organic resins while compressing in a mold of the desired shape. Such non-conducting cathode supports may then be rendered electrically conducting by immersing in solutions which permit the pores to be lined with conducting substances. By way of illustration a sintered polystyrene support may be dipped in a dilute solution of formaldehyde, followed by dipping in a second dilute solution containing silver nitrate. Such a cathode may then be coated with a deposit of the selected oxygen-activating catalyst.

Cathodes may be prepared which embody oxygen-activating catalyst selected from metals of Group VIII of the Periodic Table, metals of Groups I-B, II-B, VI-B, and VIII-B of the Periodic Table and mixtures of oxides of iron, cobalt, and nickel; spinels, perovskites, and Group VIII metals coated with oxides of trivalent metals.

Oxygen electrodes fabricated thusly are employed as cathodes in electrolytic cells having anodes fabricated of any suitable anode material, notably graphite. An oxygen-bearing gas, notably air, is applied to the cathode at a pressure just sufficient to cause bubbles to appear on the surface of an electrode when immersed in electrolyte. This pressure varies slightly depending on the pore size of the cathode and the brine concentration of the electrolyte. However, under virtually all conditions of temperature, pressure, concentration, and pore size, an excess of pressure of from 0.01 to 0.5 atmospheres is preferred.

The distance between the anode and cathode is maintained as small as possible to permit liquid circulation without resulting in current interruption by large gas pockets; the gap is conveniently maintained between 0.25 inch and 1.0 inch. Cell operation is carried out at an anode current density of from 5 to 1000, preferably from 20 to 100 amperes per square foot. The cathode current density is maintained from 5 to 100, preferably 10 to 50 amperes per square foot.

Electrolyte consisting of brine of the appropriate metal halide is passed through the cell at a rate of from 3 to 20 liters per hour per square foot of anode surface. When the alkali metal halide is sodium chloride a typical concentration is 125 grams per liter of solution, however, this may be varied considerably. By way of illustration it is often desirable to cool the electrolyte from the cell to deposit product, viz., sodium chlorate, isolate the sodium chlorate by filtration, restore the concentration of the depleted electrolyte with chloride and re-electrolyze. A suitable recycled brine for production of sodium chlorate may contain 300 grams per liter of sodium chloride and 500 grams per liter of sodium chlorate.

In the utilization of the cathodes of this invention an aqueous solution of sodium chloride or other brine of an alkali metal chloride is electrolyzed with direct current. Chlorine gas is liberated at the anode and allowed to mix with the electrolyte as a result of stirring produced by other escaping gases, i.e., hydrogen at the cathode and oxygen at the anode. The interaction with chlorine may be aided by agitation or by circulating electrolyte. As in the case of the conventional chlorate process, hypochlorite is formed by the reaction of chlorine gas with both hydroxide ion and water. Additional oxidation of the hypochlorite to chlorate by electrolysis is minimized by the stirring action which removes hypochlorite ion from the vicinity of the anode. Likewise, the desired chemical action is aided by maintaining the pH between 5 and 9, preferably between 6 and 7, to reduce the concentration of actual hypochlorite ion present.

An aqueous brine solution for use in the practice hereof, may be provided by dissolving solid alkali metal chloride in water, or may be provided from natural brine sources, or in other ways apparent to those skilled in the art. It is preferred that a brine solution is provided which is free from heavy metal impurities that tend to deposit sludge in electrolytic cells, and certain of which poison air-cathodes. Corresponding brines of alkali metal halides other than sodium chloride, may also be employed herein, subject to similar limitations on purity. Potassium chloride brine specifically may be employed in the practice of this invention. Alkali metal halides other than alkali metal chlorides are not usually economical. Thus, the preferred embodiments of the invention employ sodium chloride and potassium chloride brines.

It is convenient to adjust the pH of the brine to between 6 and 7 by the addition of hydrochloric acid. The quantity of acid required is trivial and often 0.1 to 1.0 grams of hydrochloric acid per liter of brine will suffice. It is necessary to maintain the pH slightly below 7 to minimize oxidation of hypochlorite ion at the anode. Permitting the pH to fall much below 6 tends to encourage the reaction of chloride ion with hypochlorous acid to liberate chlorine gas. Thus, while the invention is operative in the range of pH 5 to 9 it is preferred that the pH be maintained between 6 and 7 for optimum results. With the pH in this range chlorate formation appears to be highly favored.

The rate of conversion of hypochlorite to chlorate increases with temperature. Consequently, it is desired to operate the cells employed in this invention at as high a temperature as is consistent with graphite anode attrition. Anode attrition becomes severe at temperatures above 70 °C. At temperatures below about 20 °C. sodium chlorate solubility decreases greatly. At 20°C. the solubility of sodium chlorate is approximately 300 grams per liter of solution. Thus, at temperatures below 20°C. there is a probability that sodium chlorate will crystallize from the solution. Hence, it is preferable to operate above 20°C. and below 70°C. When loss of graphite can be economically tolerated, temperatures above 70°C. may be employed.

Anodes for use in the embodiment of this invention may be any inert material, such as platinum, graphite, platinum-plated copper, platinum-plated titanium, or other platinum metals, or base metals coated with platinum metal by electroplating or otherwise depositing thereon.

The invention may be better understood by reference to the following examples:

Example 1

A porous carbon cathode fabricated from Stackpole Carbon Company material, Stackpole 139 was provided with a hollowed interior by drilling a vertical hole in the cylindrical electrode. This was fitted with a tube supplying air to the interior and an electrical connection. While raising and lowering the air pressure to alternately draw electrolyte into the pores and expell electrolyte therefrom at two-minute intervals, platinum was electroplated therein over a thirty-minute period from a 1 per cent platinum chloride by weight plating solution at a current density of 40 milliamperes per square centimeter. This cathode was positioned at the center of a torroidal graphite anode to provide 0.25 inch space between anode and cathode. Electrolyte containing 300 grams of sodium chloride per liter was passed through the cell at 300 milliliters per hour. The pH was adjusted to 6.5 by the dropwise addition of 1-normal hydrochloric acid.

An electric current was applied and the temperature adjusted to 45°C. and the current was adjusted to 31 amperes per square foot of cathode surface.

Other cathodes were substituted for the air-cathode. Table I indicates the observed cell voltage.

Table 1

Cathode	Current Density Amperes per Square Foot	Observed Cell Potential Volts
"Air-Cathode"	31	1.7
Steel	31	2.9 - 3
Porous Carbon	31	2.9 - 3

Example II

A cathode was prepared as in Example 1 but was coated with calcium hydroxide by adding 0.1 gram of calcium chloride per liter of electrolyte. The following data was obtained after 72 hours of operation at 45°C.

Cell Potential, volts	1.72- 1.97
Brine Analysis, fed	
Sodium Chloride, grams per liter	302
Calcium Chloride, grams per liter	0.1
Brine Analysis, withdrawn	
Sodium Chloride, grams per liter	264.5
Calcium Chloride, grams per liter	0.05
Sodium Chlorate, grams per liter	9.65
Sodium Hypochlorite, grams per liter	1.72
Current Density, amperes per square foot	31
Current Efficiency On Chloride Consumed, per cent	89.0

Example III

An air-electrode was prepared by employing porous carbon as in Example 1 in a different procedure. The electrode was soaked fourteen hours in 10 per cent chromium nitrate by weight aqueous solution. Following the soaking treatment, the electrode was heated in an oven to decompose the nitrate to chromic oxide for two hours at 250°C. Thereafter, the plating procedure of Example 1 was applied. The cell was operated at a potential of 1.68 to 2.02 volts compared with a potential of 2.93 to 3.0 volts when operated with a steel cathode. After 72 hours the power consumption was calculated to be 2.13 and 2.79 kilowatt-hours per pound of sodium chlorate, respectively.

Example IV

An air-cathode was prepared as in Example 1 with palladium chloride substituted for platinum chloride. The 1 per cent by weight aqueous palladium chloride solution was electrolyzed at 0.04 amperes per square centimeter for 30 seconds. The cell potential resulting was 2.7 to 2.85 volts over a 96-hour period and current efficiency based on chloride consumed was 78 per cent.

Example V

A cathode was prepared as in Example 1 substituting silver nitrate for platinum chloride therein. An aqueous solution containing 10 per cent by weight silver nitrate was electrolyzed during three one-minute intervals at a current density of 10 milliamperes per square centimeter. Between platings the cathode was rinsed with distilled water. Activation was accomplished by oxidation at 20 milliamperes per square centimeter while drawing 3 per cent aqueous sodium hydroxide through the electrode during a ten-minute period. The cell operated at a potential of 2.01 to 2.65 volts for 43 hours.

In utilization of the herein described invention best economy may be realized when the concentration of sodium chloride is maintained reasonably high, i.e., 125 grams of sodium chloride per liter of brine. Below this level electrolysis to hypochlorite is satisfactory but cell potential increases and the risk of forming perchlorate becomes substantial at less than 50 grams of sodium chloride per liter of brine. Above 125 grams of sodium chloride per liter of brine, the risk of discharging free chlorine increases. Thus, from 50 to 200 grams of sodium chloride per liter of brine is the useful range and 90 to 170 grams of sodium chloride per liter of brine is preferred.

In embodiments involving the recycling of brine, it is not practical to remove all sodium chlorate before recycle. Hence brine is recycled which contains substantial concentrations of both sodium chloride and sodium chlorate. In the interest of current efficiency, it is most expeditious to convert only approximately 20 per cent of the chloride content. Thus, a brine containing 125 grams of sodium chloride per liter is electrolyzed to reduce the brine to 100 grams of sodium chloride per liter while 25 grams of sodium chloride is converted to an additional 46.5 grams of sodium chlorate. Where it is desired to separate the product by cooling the electrolyzed brine to crystallize the product therefrom, an initial sodium chlorate concentration must be present of sufficient magnitude that together with the newly formed sodium chlorate the total will fall just short of saturation at the cell operation temperature. The liquor need be cooled only sufficient after electrolysis to deposit the newly formed 46.5 grams of sodium chlorate. Salt to replace the 25 grams of sodium chloride converted is then dissolved in the reclaimed mother liquor and the cycle repeated. While one preferred practice is described thusly, many other practices can be described. However, the invention may be practiced by electrolyzing brine containing from 50 grams of sodium chloride to 310 grams per liter and sodium chlorate from nil to 800 grams per liter.

Similar considerations apply to embodiments wherein potassium chloride is electrolyzed to form potassium chlorate. However, different solubility relationships apply and the concentrations during electrolysis are approximately the same on a molar basis as those involving sodium chloride.

SUPPLEMENTARY DISCLOSURE

The Principal Disclosure related to the manufacture of alkali metal chlorates by an improved electrolytic process, by reactions expressed by the equations

$$2\ Cl^- \longrightarrow Cl_2 + 2e$$
$$Cl_2 + 2\ OH^- \longrightarrow ClO^- + H_2O$$
$$Cl_2 + H_2O \longrightarrow HClO + Cl^- + H^+$$
$$2\ HClO + ClO \longrightarrow ClO_3^- + 2\ Cl^- + 2H^+$$

The last reaction is favored by high temperature and requires no electric current to result in chlorate formation. Operation of commercial cells is carried out in an acid environment to favor formation of HClO and avoid the anode reaction which is promoted by high pH as follows:

$$6\ ClO^- + 3\ H_2O \longrightarrow 2\ ClO_3 + 1.5\ O_2 + 4\ Cl^- + 6\ H^+ + 6_e$$

Alternatively, the reactions occurring in this process may be expressed by the following equations:

(1) $$3\ Cl_2 + 60H^- \longrightarrow 3\ ClO^- + 3Cl^- + 3H_2O$$

(2) $$2ClO^- + 2H^+ \rightleftarrows 2HClO$$

(3) $$2HClO + ClO^- \longrightarrow ClO_3^- + 2Cl^- + 2H^+$$

The overall chemical reaction may be expressed as:

(4) $$3Cl_2 + 60H^- \longrightarrow ClO_3^- + 5Cl^- + 3H_2O$$

Operation of commercial cells is carried out in an acid environment to favor formation of HClO as indicated by reversible equation (2). In general, graphite anodes and steel cathodes are employed to result in a potential drop across the cell of 3.5 to 3.7 volts.

The Principal Disclosure provided a method for the production of alkali metal chlorate which comprises electrolysis of brine containing a substantial concentration of alkali metal chloride between chemically inert anodes and cathodes of electrically conducting oxygen-activating catalyst on chemically inert porous substrate, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere. According to the invention provided by the present Supplementary Disclosure, a method has been developed for the production of alkali metal chlorates, notably sodium chlorate, which comprises electrolyzing brine containing

A B

a substantial concentration of alkali metal chloride, notably sodium chloride, at a pH of 5 to 9, preferably 6 to 7, and a preferable temperature of 20°C. to 70° C., while oxygen-bearing gas is provided at the electrolyte-electrode interface.

Air cathodes may also be fabricated with spinel deposition. An aqueous solution of mixed soluble salts is utilized to deposit a coating of the salts on a porous carbon cathode when it is dipped therein. The treated electrode is then heated red hot to result in the formation of mixed metal oxides having the characteristic crystalline structure of spinels. By way of illustration, an impregnating solution of ferric nitrate and magnesium nitrate is prepared. A porous carbon cathode is dipped into this solution and vacuum is applied on the hollow interior. After a suitable length of time the cathode is removed and heated to about 110°C., preferably in an oven to prevent hot spots. When the deposited layer has dried, this procedure may be repeated a few times to build up the deposit. The duration and frequency of the soak depends upon the particular deposit desired. Commonly, the cathode is soaked a total of a few hours and dried between each successive application; however, a soak of as short as about ten minutes will suffice as long as the cathode is completely saturated therefrom. Alternatively, the cathode may be placed in the soak solution and a vacuum applied over the solution containing the cathode.

When a suitable deposit has been applied, the cathode may be heated for a short time in an oxygen-illuminated gas flame or other suitable heating arrangement to a temperature of approximately 1200°C. A mixed magnesium iron oxide deposit results which has the characteristic crystalline structure of magnesium iron spinel. Similar results may be obtained by application of an oxide paste or aqueous slurry prior to ignition.

Any spinel may be employed in the practice of this invention. The spinel group of minerals encompasses a vast number of possibilities. Although one skilled in the art could readily perceive of many spinels, the following lists some of them. It is to be understood that the invention is not to be limited to embodiments employing only these specific spinels but that the scope of the invention includes all possible spinel catalysts.

$NiFe_2O_4$
$NiCr_2O_4$
$ZnAl_2O_4$
$MnCr_2O_4$
$ZnCr_2O_4$
$MgFe_2O_4$
$FeAl_2O_4$
$MgAl_2O_4$
$MnAl_2O_4$
$MgCr_2O_4$
$LiFe_5O_8$
$CuAl_5O_8$
$CuFe_5O_8$
$CuCr_5O_8$
$CuAl_2O_4$
$NiAlFeO_4$
$MaIn_2S_4$
Cu_2FeO_4
$CuCr_2O_4$
$LiAlTiO_4$
$LiFeTiO_4$
$LiCrTiO_4$
$NiCrFeO_4$
$ZnCr_2S_4$
$CuAlTiO_4$
$CuFeTiO_4$
$CuCrTiO_4$
$MgAlFeO_4$
$MgCrFeO_4$
$2Li_2O.7TiO_2$ etc.

Spinels are, in essence, fused mixtures of di and tri valent metal oxides. There exists three main spinel types: (1) A^{2+}, B^{3+}, designated 2:3, (2) A^{4+}, B^{2+}, 4:2; and (3) A^{6+}, B^{1+}, 6:1 where A and B are metal cations. The most stable and, hence, most common structure is the 2:3 type or the binary-metal oxide of the general type AB_2O_4, where A and B represent the metal cation, some of which are given in the hereinbefore contained list.

In the practice of this invention it is common to employ an additive in the cell liquor when the oxygen-activating catalyst is a spinel. These additives increase the overall efficienty of the cell. This additive is generally a metal salt with the metal corresponding to one of the metals comprising the spinel. By way of example, if a magnesium iron spinel is used as the oxygen-activating catalyst, magnesium halide may be used as the additive. Alternately, mixed magnesium and iron halides may be used to advantage as additives. Similarly, metal salts corresponding to any of the utilized spinels may be employed.

Additives include any salt of the corresponding spinel metals, however it is advantageous to employ the metal halides. Mixed additives of salts of both spinel metals may be employed. These additives may be in any concentration but preferably 0.5 to 5.0 grams per liter of electrolyte. Lower concentrations may prove inadequate for extended use of the cell. Higher concentration may project an economic disadvantage.

The following are additional Examples of the present invention.

EXAMPLE II

An air cathode was prepared as in Example I. The following data was obtained after 192 hours of operation at 65°C.

Current density, amperes per square foot of cathode surface	22
Air pressure, atmospheres	0.5-0.7
Brine Analysis, fed	
Sodium chloride, grams per liter of electrolyte	171
Magnesium chloride, grams per liter of electrolyte	2
Sodium chlorate, grams per liter of electrolyte	398
Cathode Potential, volts	0.54-0.27
Cell Potential, volts	2.35-2.05
Brine Volume, liters	
Start	2.0
End	2.8
Brine Analysis, withdrawn	
Sodium Chloride, grams per liter of electrolyte	100
Sodium Chlorate	333
Sodium Hypochlorite	1.1
Current Efficiency on Chlorate Produced, per cent	83.6

EXAMPLE III

An air cathode was prepared as in Example I except a zinc chromium spinel was deposited by alternately raising and lowering the pressure within the porous carbon support while the carbon support was dipped in an aqueous solution 10 per cent by weight chromium nitrate and 4 percent by weight zinc nitrate. A final ignition to about 1200°C. for one minute formed the mixed oxide spinel. Added to the brine before electrolysis was mixed additives of chromic chloride and zinc chloride. A current density of 30 amperes per square foot of cathode surface for 48 hours resulted in a cell potential of 2.4 volts compared to 3.2 volts when a steel cathode was used.

EXAMPLE IV

An air cathode was prepared as in Example I with nickel nitrate and chromium nitrate substituted for the magnesium and ferric nitrates employed therein. Using this cathode in the cell of Example I and operating under the conditions of Example I for 48 hours, a current efficiency based on chlorate produced of 72 per cent was obtained.

EXAMPLE V

An air cathode was prepared as in Example II and it was employed in an identical cell except that the temperature was maintained at 45°C. and the current density at 30 amperes per square foot of cathode surface. One gram magnesium chloride per liter of electrolyte was used in the cell. After 75 hours at a cell potential of 2.07 to 2.02 volts and a cathode potential of 0.40 to 0.36 volt a 74 per cent current efficiency based on chlorate produced was realized compared with respective voltages of 3.36 to 3.21 and 1.27 to 1.19 and a current efficiency, based on chlorate produced, of 59 per cent with a carbon cathode embodiment.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for the production of alkali metal chlorate which comprises electrolysis of brine containing a substantial concentration of alkali metal chloride between chemically inert anodes and cathodes of electrically conducting oxygen-activating catalyst on chemically inert porous substrate, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

2. A method for the production of alkali metal chlorate which comprises electrolysis of brine containing a substantial concentration of alkali metal chloride between chemically inert anodes and cathodes of oxygen-activating platinum group metal on porous carbon, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

3. A method for the production of alkali metal chlorate which comprises electrolysis of brine containing a substantial concentration of alkali metal chloride between, chemically inert anodes and cathodes of oxygen-activating platinum metal on porous carbon, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

4. A method for the production of alkali metal chlorate which comprises electrolysis of brine containing a substantial concentration of alkali metal chloride between chemically inert anodes and cathodes of oxygen-activating chromic oxide on porous carbon, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

5. A method for the production of sodium chlorate which comprises electrolysis of brine containing a substantial concentration of sodium chloride between graphite anodes and

cathodes of electrically conducting oxygen-activating catalyst on chemically inert porous substrate, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

6. A cyclic process for the manufacture of sodium chlorate wherein brine containing a substantial concentration of sodium chloride is electrolyzed between a graphite anode and a cathode of electrically conducting oxygen-activating catalyst on chemically inert porous substrate, the interface of which is supplied through adventitious pores with oxygen from an oxygen-bearing atmosphere.

CLAIMS SUPPORTED BY THE SUPPLEMENTARY DISCLOSURE

7. A method for the production of alkali metal chlorate which comprises electrolyzing brine containing 50 to 310 grams per liter alkali metal chloride and up to 800 grams per liter alkali metal chlorate in an electrolytic cell containing chemically inert anodes and cathodes, the cell cathodes comprising electrically conducting oxygen-activating catalyst on a chemically inert porous substrate, and also containing metal salt additive, and supplying to the interface of said cathodes and said brine through adventitious pores in the cathodes oxygen from an oxygen-bearing atmosphere, and crystallizing a portion of the thus formed alkali metal chlorate by cooling the electrolyzed brine.

8. A method for the production of alkali metal chlorate which comprises electrolyzing brine containing 50 to 310 grams per liter alkali metal chloride and up to 800 grams per liter alkali metal chlorate in an electrolytic cell containing chemically inert anodes and cathodes, the cell cathodes comprising electrically conducting oxygen-activating spinel on a chemically inert porous substrate, and also containing a member of the group consisting of (a) metal salt additive and (b) mixed metal salt additives, a metal of said member corresponding to at least one of the metals comprising the spinel, and supplying to the interface of said cathodes and said brine through adventitious pores in the cathodes oxygen from an oxygen-bearing atmosphere, and crystallizing a portion of the thus formed alkali metal chlorate by cooling the electrolyzed brine.

9. The method of Claim 8 wherein the said spinel is a magnesium iron spinel and the said additive is a magnesium halide.

10. The method of Claim 8 wherein the said spinel is a zinc chromium spinel and the said additive is a mixture of zinc and chromium halides.

11. The method of Claim 8 wherein the said spinel is a nickel chromium spinel and the said additive is a mixture of nickel and chromium halides.

12. A method for the production of sodium chlorate which comprises electrolyzing brine containing 50 to 310 grams per liter sodium chloride and up to 800 grams per liter sodium chlorate in an electrolytic cell containing chemically inert anodes and cathodes, the cell cathodes comprising electrically conducting oxygen-activating spinel on porous carbon, and also containing metal salt additive, and supplying to the interface of said cathodes and said brine through adventitious pores in the cathodes oxygen from an oxygen-bearing atmosphere, and crystallizing a portion of the thus formed sodium chlorate by cooling the electrolyzed brine.

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SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente