Notice

DESCRIPTION JP5755997B2

Perchlorate manufacturing apparatus and perchlorate manufacturing method

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[0001]

The present invention relates to an apparatus for producing perchlorate and a method for producing perchlorate.

[0002]

Conventionally, a method for industrially producing perchlorates has been known in which a voltage is applied to an aqueous solution of sodium chloride (NaCl) to perform electrolysis (electrolytic oxidation) to synthesize sodium chlorate ($NaClO_3$), and the resulting aqueous solution of sodium chlorate is further electrolytically oxidized to synthesize sodium perchlorate ($NaClO_4$) (for example, Non-Patent Document 1). In a conventional method, when producing a perchlorate other than sodium perchlorate, for example, ammonium sulfate ((NH ₄) ₂ SO ₄) is added to the sodium perchlorate obtained by the above method, and ammonium perchlorate (NH ₄ ClO ₄) can be synthesized by a double decomposition reaction.

[0003]

Also disclosed is a technology for producing a perchlorate other than sodium perchlorate (hereinafter simply referred to as perchlorate) without going through sodium perchlorate by using an electrolytic cell in which an anode cell having an anode and a cathode cell having a cathode are separated by a cation exchange membrane, storing an aqueous sodium chloride solution or an aqueous sodium chlorate solution in the anode cell, while storing pure water in the cathode cell, and performing electrolysis (see, for example, Patent Document 1).

[0004]

Specifically, in the technology of Patent Document 1, chlorine (Cl ₂) is synthesized in an anode tank by electrolytic oxidation of a sodium chloride aqueous solution, and then hypochlorous acid (HClO ₂) is synthesized by an equilibrium reaction between chlorine and water, and the synthesized hypochlorous acid is further electrolytically oxidized to synthesize chlorous acid (HClO ₂), chloric acid (HClO ₃), and then perchloric acid (HClO ₄).

When an aqueous solution of sodium chlorate is electrolytically oxidized in the anode tank, perchloric acid is synthesized.

[0005]

Then, by adding carbonates such as potassium carbonate (K ₂ CO ₃), lithium carbonate (Li ₂ CO ₃), or ammonium carbonate ((NH ₄) ₂ CO ₃), or hydroxides such as potassium hydroxide (KOH), lithium hydroxide (LiOH), or ammonia water or ammonia gas to the strongly acidic anode solution having a pH of 2.3 or less and containing perchloric acid as the main component after the electrolytic oxidation, perchlorates such as potassium perchlorate (KClO ₄), lithium perchlorate (LiClO ₄), and ammonium perchlorate can be synthesized by a neutralization reaction.

[0006]

The technology of Patent Document 1 uses an electrolytic cell in which an anode cell in which an anode is provided and a cathode cell in which a cathode is provided are separated by a cation exchange membrane, so that it is possible to avoid a situation in which hypochlorous acid, chlorous acid, chloric acid, and perchloric acid synthesized at the anode provided in the anode cell are reduced at the cathode provided in the cathode cell.

Therefore, by using the technology of Patent Document 1, it becomes unnecessary to add an anti-reducing agent (sodium dichromate) to the aqueous solution, which was required in the method described in Non-Patent Document 1.

Furthermore, in the technology of Patent Document 1, the target perchlorate is synthesized by a neutralization reaction in which the by-product is water.

Therefore, the technique of Patent Document 1 does not require the separation step required in the technique of Non-Patent Document 1, which is to separate the target perchlorate from the crystalline by-product produced by the metathesis reaction.

[0007]

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[0008]

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[0009]

However, in the technique of Patent Document 1 described above, not all of the sodium ions (Na [＋]) contained in the anode solution are transferred to the cathode tank during electrolysis.

Therefore, sodium ions remain in the strongly acidic anolyte solution containing perchloric acid as the main component and having a pH of 2.3 or less after electrolytic oxidation.

Here, most of the sodium ions in the anode solution remain in the filtrate in the crystallization step when the perchlorate is crystallized.

However, some of the sodium ions in the anode solution may be mixed as impurities into the target perchlorate.

For example, when ammonium perchlorate is synthesized as the target product, it may be incorporated into ammonium perchlorate crystals as a substitution atom for the ammonium ion.

It may also adhere to the surface of ammonium perchlorate crystals.

[0010]

Thus, when electrolysis is performed using the technique of Patent Document 1, which uses an aqueous sodium chloride solution or an aqueous sodium chlorate solution as a raw material, sodium ions remain in the anode solution after electrolytic oxidation.

As a result, the purity of the target perchlorate may decrease.

Therefore, when crystallizing the target perchlorate, it is desired to reduce the sodium ions in the aqueous anode solution having a pH of 2.3 or less and containing perchloric acid as the main component after the electrolytic oxidation.

[0011]

In view of the above problems, the present invention has an object to provide a perchlorate manufacturing apparatus and a perchlorate manufacturing method that can reduce the concentration of sodium ions in a strongly acidic anode solution containing perchloric acid as a main component and having a pH of 2.3 or less after electrolytic oxidation, in which sodium ions remain, by precipitating and removing the sodium ions as carbonate.

[0012]

In order to solve the above problems, the perchlorate manufacturing apparatus of the present invention is characterized by comprising: an electrolytic cell in which an anode cell containing an aqueous solution containing at least one ion selected from chloride ions, hypochlorite ions, chlorite ions, and chlorate ions, and alkali metal ions and having an anode, and a cathode cell containing H_2O and having a cathode, are separated by a cation exchange membrane; a DC stabilized power supply for applying a voltage to the anode and cathode; a basic compound introduction section that introduces a basic compound into a strongly acidic anode solution having a pH of 2.3 or less and containing perchloric acid as the main component generated in the anode cell by electrolytic oxidation, thereby adjusting the pH of the anode solution to 12.0 or higher; and a carbon dioxide introduction section that introduces carbon dioxide into the alkaline anode solution whose pH has been increased to 12.0 or higher.

[0014]

The basic compound is preferably a compound selected from carbonates, hydroxides, and ammonia.

[0015]

More preferably, the basic compound is a compound selected from ammonium carbonate (NH ₄ CO ₃), lithium carbonate (Li ₂ CO <sub> 3 < /sub>), potassium carbonate (K ₂ CO ₃), lithium hydroxide (LiOH), potassium hydroxide (KOH), aqueous ammonia (NH ₄ OH), or ammonia (NH ₃).

[0016]

In order to solve the above-mentioned problems, the present invention provides a method for producing perchlorate using an electrolytic cell in which an anode cell containing an aqueous solution containing at least one ion selected from chloride ions, hypochlorite ions, chlorite ions, and chlorate ions, and alkali metal ions and having an anode, and a cathode cell containing H_2O and having a cathode, are separated by a cation exchange membrane, and a DC stabilized power supply for applying a voltage to the anode and cathode. The method is characterized by comprising: an electrolysis step in which a voltage is applied to the anode and cathode using the DC stabilized power supply; an alkalinization step in which a basic compound is introduced into a strongly acidic anode solution having a pH of 2.3 or less and containing perchloric acid as the main component, generated in the anode cell by electrolytic oxidation, to adjust the pH of the anode solution to 12.0 or higher; and a step in which carbon dioxide is introduced into the alkaline anode solution whose pH has now reached 12.0.

[0017]

According to the present invention, a basic compound is added to a strongly acidic anode solution having a pH of 2.3 or less and containing perchloric acid as the main component after electrolytic oxidation to alkalinize the aqueous solution, and then carbon dioxide (CO_2) is introduced into the solution, thereby precipitating and removing the alkali metal ions as carbonates.

This reduces the concentration of alkali metal ions remaining in the strongly acidic anolyte solution containing perchloric acid as a main component after the electrolytic oxidation, making it possible to produce a highly pure perchlorate.

[0018]

FIG. 1 is an explanatory diagram for explaining a schematic configuration of an apparatus for manufacturing perchlorate according to an embodiment.

FIG. 2 is an explanatory diagram for describing a specific configuration of a primary electrolysis unit.

FIG. 1 is a diagram showing the relationship between the form of hypochlorous acid and pH.

FIG. 2 is an explanatory diagram for explaining a specific configuration of a secondary electrolysis unit.

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1 is a flowchart illustrating a process flow of a method for producing a perchlorate according to an embodiment.

FIG. 2 is an explanatory diagram for explaining the state of a valve in each step of a method for producing a perchlorate salt.

[0019]

Preferred embodiments of the present invention will be described in detail below with reference to the accompanying drawings.

The dimensions, materials, and other specific numerical values shown in these embodiments are merely examples to facilitate understanding of the invention, and do not limit the present invention unless otherwise specified.

In this specification and drawings, elements having substantially the same functions and configurations are designated by the same reference numerals to avoid redundant explanation, and elements not directly related to the present invention are not shown.

[0020]

Perchlorates, which have strong oxidizing power, are used in a variety of fields.

For example, ammonium perchlorate is used as an oxidizer in solid fuel rocket propellants, and potassium perchlorate is used as an oxidizer in airbag ignition agents.

[0021]

The final composition containing perchlorate contains small amounts of impurities.

Such impurities include sodium salts derived from the raw materials sodium chloride and sodium chlorate.

[0022]

For example, when ammonium perchlorate is synthesized using sodium chloride as a raw material, impurities such as sodium chloride, sodium hypochlorite, sodium chlorate, and sodium perchlorate may be contained.

When this final synthesis product is used as an oxidizer for a solid fuel rocket propellant, the sodium salt mixed in the ammonium perchlorate as an impurity promotes the thermal decomposition of the nozzle that constitutes the solid fuel rocket.

Therefore, when the content of sodium salt in ammonium perchlorate is high, the nozzle plate thickness needs to be made thicker than when the content of sodium salt is low.

[0023]

Therefore, in this embodiment, an apparatus and a method for producing a perchlorate will be described that can improve the purity of the target perchlorate by precipitating and removing alkali metal ions derived from raw materials that may be contained as impurities in the target product as carbonates.

[0024]

(Perchlorate Manufacturing Apparatus 100) FIG. 1 is an explanatory diagram for explaining the schematic configuration of a perchlorate manufacturing apparatus 100 according to this embodiment.

As shown in FIG. 1 , the perchlorate manufacturing apparatus 100 includes a primary electrolysis unit 200, a secondary electrolysis unit 300, a basic compound introducing section

400, a carbon dioxide introducing section 450, a reaction tank 490, and a crystallization tank 492.

In FIG. 1, the flow of gas is indicated by dashed arrows, the flow of liquid is indicated by solid arrows, and the flow of solids is indicated by dashed arrows.

As an example, the synthesis of ammonium perchlorate as the target product will be described here using sodium chloride, which is inexpensive and easily available as a raw material.

[0025]

(Primary electrolysis unit 200) FIG. 2 is an explanatory diagram for describing a specific configuration of the primary electrolysis unit 200.

As shown in FIG. 2 , the primary electrolysis unit 200 includes an electrolytic cell 210 , an anode solution reservoir 250 , a cathode solution reservoir 252 , and a regulated DC power supply 260 .

[0026]

The electrolytic cell 210 is composed of an anode cell 220 and a cathode cell 230 , and the anode cell 220 and the cathode cell 230 are separated by a cation exchange membrane 240 .

The pH of the primary anode solution (anode side solution) in the electrolytic cell 210 ultimately becomes acidic, ranging from 2.3 to 5.0, due to electrolytic oxidation.

On the other hand, the pH of the cathode solution (cathode side solution) in the electrolytic cell 210 becomes alkaline due to reduction.

The pH of the cathode solution depends on the amount of H ₂ O introduced into the cathode solution reservoir 252 (described later), and is generally strongly alkaline, at 12.0 or higher.

Therefore, the body of the electrolytic cell 210 and the joints of the piping should preferably be made of a material that is highly stable against chemicals, such as Teflon (registered trademark), vinyl chloride, or glass.

[0027]

A sodium chloride aqueous solution (NaCl(aq)) is supplied to the anode tank 220 from an anode solution reservoir 250 (described later) through a pipe 250b.

The anode tank 220 contains an aqueous sodium chloride solution and is provided with an anode 222 .

[0028]

The anode 222 is made of an expanded metal coated with a catalyst that promotes the electrolytic oxidation reaction of chloride ions (Cl [−]) in the anode tank 220 .

Specifically, the anode 222 is made of a titanium expanded metal substrate whose surface is coated with a catalyst that suppresses the generation of oxygen gas by a baking method.

Examples of catalysts that have the effect of suppressing the generation of oxygen gas include iridium oxide and platinum, iridium oxide, ruthenium oxide and platinum, and tantalum oxide and platinum.

[0029]

H_2O is supplied to the cathode tank 230 from a cathode solution reservoir 252 (described later) through a pipe 252b.

The cathode tank 230 contains H_2O and is provided with a cathode 232 .

[0030]

The cathode 232 is made of, for example, an expanded metal or an expanded metal whose surface is coated with a catalyst.

Specifically, nickel expand metal or titanium expand metal coated with platinum by electrolytic plating is used as the cathode 232 .

[0031]

The cation exchange membrane 240 is sandwiched between the anode 222 and the cathode 232 in the electrolytic cell 210 with substantially no gap between them.

By configuring the cation exchange membrane 240 in this manner, the electrolytic cell 210 becomes a zero-gap type electrolytic cell.

The cation exchange membrane 240 is a membrane that has the property of allowing cations to pass through but not allowing anions to pass through.

The cation exchange membrane 240 may be made of, for example, Nafion (registered trademark), Aciplex (registered trademark), or Flemion (registered trademark).

[0032]

A sodium chloride aqueous solution is introduced into the anode solution reservoir 250 through an introduction pipe 250a from an anode raw material source (not shown).

The aqueous solution introduced into the anode solution reservoir 250 is not limited to a sodium chloride aqueous solution as long as it contains sodium ions and at least one ion selected from chloride ions, hypochlorite ions (ClO^{-}), or chlorite ions (ClO_2^{-}).

[0033]

The anode solution reservoir 250 is connected to the anode tank 220 by pipes 250b and 250c.

Pipe 250b is a pipe that connects the lower side wall of the anode tank 220 and the lower side wall of the anode solution reservoir 250, and pipe 250c is a pipe that connects the top surface of the anode tank 220 and the side wall of the anode solution reservoir 250.

[0034]

The flow of the aqueous sodium chloride solution and the primary anolyte solution AS1 will be described.

The aqueous sodium chloride solution introduced into the anode solution reservoir 250 is supplied to the anode tank 220 through a pipe 250b.

Then, a voltage is applied to the anode 222 and the cathode 232 using a DC stabilized power supply 260 described below, thereby oxidizing chloride ions in the aqueous sodium chloride solution in the anode tank 220 and producing a primary anode solution AS1.

The primary anolyte solution AS1 is again led to the anolyte reservoir 250 via the pipe 250c.

Thereafter, the primary anolyte solution AS1 undergoes the above-described cycle repeatedly, and becomes an aqueous solution containing chloric acid as the main component, passing through hypochlorous acid and chlorous acid.

[0035]

The anode solution reservoir 250 is also provided with an inlet pipe 250d for introducing a compound (e.g., sodium hydroxide) for adjusting the pH of the anode solution AS1 or an aqueous solution (e.g., aqueous sodium hydroxide solution) for adjusting the pH of the anode solution AS1.

The primary anolyte solution AS1 contained in the anolyte reservoir 250 and the anolyte tank 220 becomes a strongly acidic aqueous solution with a pH of about 1 through electrolytic oxidation.

Therefore, in order to prevent the generation of chlorine gas or chlorine dioxide (ClO ₂) gas caused by a decrease in the pH of the primary anode solution AS1, the above compound or the above aqueous solution is introduced into the anode solution reservoir 250 through the introduction pipe 250d.

As a result, the primary anolyte solution AS1 finally becomes an acidic aqueous solution with a pH of 2.3 to 5.0.

Furthermore, an exhaust pipe 250e is provided on the top surface of the anode solution reservoir 250 for exhausting oxygen (O ₂) and ozone (O ₃) that may be generated at the anode 222 during electrolytic oxidation of the sodium chloride aqueous solution to the outside.

[0036]

Furthermore, the anode solution reservoir 250 communicates with an anode tank of a secondary electrolysis unit 300 (described later) via an AS1 delivery pipe 256a and a valve 258a.

This AS1 delivery pipe 256a is connected to the lower side wall of the anode solution reservoir 250, opposite the lower side wall to which the anode tank 220 is connected.

[0037]

H_2O (for example, pure water) is introduced into the cathode solution reservoir 252 from a cathode material source (not shown) through an inlet pipe 252a.

Here, the H ₂ O introduced into the cathode solution reservoir 252 may be pure water or an aqueous solution.

[0038]

The cathode solution reservoir 252 is connected to the cathode tank 230 by pipes 252b and 252c.

The pipe 252b is a pipe that connects the lower side wall of the cathode tank 230 and the lower side wall of the cathode solution reservoir 252, and the pipe 252c is a pipe that connects the top surface of the cathode tank 230 and the side wall of the cathode solution reservoir 252.

[0039]

Here, the flow of H_2O and the catholyte solution CS will be explained.

The H_2O introduced into the cathode solution reservoir 252 is supplied to the cathode tank 230 through a pipe 252b.

Then, by applying a voltage to the anode 222 and the cathode 232 using a DC stabilized power supply 260, protons (H^+) generated at the anode 222 and sodium ions in the anode solution move from the anode tank 220 to the cathode tank 230 through the cation exchange membrane 240, and are reduced to hydrogen (H_2) and sodium hydroxide at the cathode 232.

Here, the hydrogen is discharged to the outside through the discharge pipe 252e.

On the other hand, sodium hydroxide dissolves in water to form an aqueous sodium hydroxide solution, which is again led to the cathode solution reservoir 252 via the pipe 252c.

Thereafter, the catholyte CS repeats the above circulation.

[0040]

Furthermore, the cathode solution reservoir 252 is provided with a CS delivery pipe 256b and a valve 258b.

The CS delivery pipe 256b is connected to the lower side wall of the cathode solution reservoir 252, opposite the lower side wall to which the cathode tank 230 is connected.

[0041]

By using a DC stabilized power supply 260, a voltage is applied to the anode 222 and the cathode 232 when the anode tank 220 contains a sodium chloride aqueous solution or a primary anode solution AS1 and the cathode tank 230 contains H ₂ O or a cathode solution CS.

[0042]

As a result, the reaction shown in the following reaction formula (1) proceeds at the anode 222.

2Cl NER52 → Cl NER53 + 2e NER54 ...Reaction equation (1)

[0043]

Furthermore, depending on the voltage application conditions, the concentration of chloride ions in the anode solution, and the temperature of the anode solution, the reaction shown in reaction formula (2) or reaction formula (3) may also proceed.

2H ₂ O → O ₂ + 4H [＋] + 4e [−] ...

Reaction formula (2) 3H _２ O → O _３ + 6H [＋] + 6e [−] ... Reaction formula (3)

[0044]

The chlorine generated by the reaction shown in reaction formula (1) proceeds, and the equilibrium reactions shown in the following reaction formulas (4) and (5) proceed.

<chemistry num="1"> </chemistry> ...Reaction equation (4) <chemistry num="2"> </chemistry> ...Reaction equation (5)

[0045]

The equilibrium reactions shown in the above reaction formulas (4) and (5) depend on the pH of the anode solution.

Therefore, in order to efficiently generate hypochlorous acid, a compound for adjusting the pH of the anode solution AS1 or an aqueous solution for adjusting the pH of the anode solution AS1 is introduced into the anode solution reservoir 250 (anode tank 220) from the inlet pipe 250d.

[0046]

FIG. 3 is a diagram showing the relationship between the form of hypochlorous acid and pH.

As shown in FIG. 3, when the pH of the solution is 5.0, the dissolved substance exists as hypochlorous acid, and chlorine and hypochlorite ions are not present.

That is, the reaction proceeds from the left side to the right side of the above reaction formula (4).

[0047]

Here, when the pH of the solution is increased from 5.0 (when the solution is made alkaline), the proportion of hypochlorous acid present gradually decreases, and the proportion of hypochlorite ions present gradually increases.

In other words, the reaction proceeds from the left side to the right side of reaction formula (5).

On the other hand, when the pH of the solution is lowered from 5.0 (when the solution becomes more acidic), the proportion of hypochlorous acid present gradually decreases and the proportion of chlorine present gradually increases.

In other words, the reaction proceeds from the right side to the left side of reaction formula (4).

[0048]

Here, in order to prevent the generation of chlorine gas in the anode tank 220, the primary anode solution AS1 is adjusted to have a pH of 5.0 or higher.

Specifically, the pH of the primary anolyte AS1 is controlled by introducing a compound for adjusting the pH of the anolyte AS1 or an aqueous solution for adjusting the pH of the anolyte AS1 from the inlet pipe 250d into the anolyte reservoir 250 (anode tank 220).

[0049]

Subsequently, when hypochlorous acid produced by electrolytic oxidation of the sodium chloride aqueous solution is electrolytically oxidized, the reaction shown in the following reaction formula (6) proceeds.

HClO + H ₂ O → HClO ₂ + 2H [＋] + 2e <sup> − < /sup> ⋯ Reaction formula (6)

[0050]

Here, in order to prevent the generation of chlorine dioxide gas in the anode tank 220, the pH of the primary anode solution AS1 is adjusted to 2.3 or higher.

Specifically, the pH of the primary anolyte AS1 is controlled by introducing a compound for adjusting the pH of the anolyte AS1 or an aqueous solution for adjusting the pH of the anolyte AS1 from the inlet pipe 250d into the anolyte reservoir 250 (anode tank 220).

[0051]

Then, the chlorous acid produced by reaction formula (6) is further electrolytically oxidized, whereby the synthesis reaction of chlorous acid shown in the following reaction formula (7) proceeds.

HClO ₂ + H ₂ O → HClO ₃ + 2H [＋] + 2e [−] ⋯Reaction formula (7)

[0052]

In this way, by applying a voltage to the anode 222 and the cathode 232 using the DC stabilized power supply 260, the reactions shown in the above reaction formulas (1) to (7) proceed in the anode tank 220.

By controlling the pH of the anolyte AS1 in the primary electrolysis, the target product, chloric acid, can be synthesized in high yield.

[0053]

The oxygen gas and ozone gas that can be generated in the anode tank 220 (see reaction formulas (2) and (3)) are introduced into the anode solution reservoir 250 through a pipe 250c.

The oxygen gas and ozone gas are then sequentially exhausted to the outside through a pipe 250 e provided on the top surface of the anode solution reservoir 250 .

In this way, the oxygen gas and ozone gas generated in the anode chamber 220 are sequentially exhausted to the outside, so that the pressure inside the anode chamber 220 becomes negative.

For this purpose, the primary anolyte AS1 is sequentially introduced from the anolyte reservoir 250 through the pipe 250b into the lower part of the anolyte tank 220.

Therefore, the primary anolyte solution AS1 can be circulated between the anolyte tank 220 and the anolyte reservoir 250 without using a driving mechanism such as a pump.

[0054]

On the other hand, sodium ions contained in the primary anolyte solution AS1 pass through the cation exchange membrane 240 due to the potential difference between the anode 222 and the cathode 232 and move from the anode chamber 220 to the cathode chamber 230.

As a result, the reactions shown in the following reaction formulas (8) and (9) proceed at the cathode 232.

2H [＋] + 2e [−] → H _２ ⋯ Reaction formula (8) 2Na [＋] + 2H _２ O + 2e [−] → 2NaOH + H _２⋯ Reaction formula (9)

[0055]

The hydrogen gas produced in the cathode tank 230 is introduced into the cathode solution reservoir 252 through a pipe 252c.

The hydrogen gas is then sequentially discharged to the outside through a pipe 252 e provided on the top surface of the cathode solution reservoir 252 .

Therefore, similar to the mechanism for circulating the primary anolyte solution AS1 described above, in the cathode tank 230 and the cathode solution reservoir 252, the cathode solution CS is sequentially introduced from the bottom of the cathode tank 230 through the pipe 252b from the cathode solution reservoir 252.

Therefore, the cathode solution CS can be circulated between the cathode tank 230 and the cathode solution reservoir 252 without using a driving mechanism such as a pump.

[0056]

As shown in the above reaction formula (7), after the chlorous acid in the primary anolyte solution AS1 is converted to chloric acid in the anode tank 220, the valve 258a is shifted from a closed state to an open state by a control device (not shown).

As a result, the primary anolyte AS1 is delivered from the anolyte reservoir 250 to the anode tank of the secondary electrolysis unit 300 through the AS1 delivery pipe 256a.

Meanwhile, the valve 258b is changed from a closed state to an open state by a control device (not shown).

As a result, the catholyte solution CS is discharged from the catholyte solution reservoir 252 to the outside through the CS delivery pipe 256b.

[0057]

(Secondary electrolysis unit 300) FIG. 4 is an explanatory diagram for explaining a specific configuration of the secondary electrolysis unit 300.

As shown in FIG. 4 , the secondary electrolysis unit 300 includes an electrolytic cell 210 , an anode solution reservoir 350 , a cathode solution reservoir 252 , and a regulated DC power supply 260 .

Note that components that are substantially equivalent in function to those of the primary electrolysis unit 200 described above are denoted by the same reference numerals, and descriptions thereof will be omitted.

[0058]

Similar to the primary electrolysis unit 200 , the electrolytic cell 210 includes an anode cell 220 and a cathode cell 230 , which are separated from each other by a cation exchange membrane 240 .

[0059]

The primary anolyte AS1 produced in the primary electrolysis unit 200 is introduced into the anode tank 220 from an anolyte reservoir 350 (described later) through a pipe 350b.

The anode tank 220 contains a primary anode solution AS1 and is provided with an anode 322 .

[0060]

The anode 322 is made of an expanded metal coated with a catalyst that promotes the electrolytic oxidation reaction of chloric acid in the anode tank 220 .

Specifically, the anode 322 is made of a titanium expanded metal substrate whose surface is coated with platinum.

[0061]

The cathode tank 230 receives H_2O (for example, pure water) from the cathode solution reservoir 252 via a pipe 252b.

Here again, the H_2O introduced into the cathode solution reservoir 252 may be pure water or an aqueous solution.

The cathode tank 230 contains H_2O and is provided with a cathode 332 .

[0062]

The cathode 332 is made of, for example, an expanded metal or an expanded metal whose surface is coated with a catalyst.

Specifically, nickel expand metal, SUS316 expand metal, or titanium expand metal coated with platinum by electrolytic plating is used as the cathode 332 .

[0063]

In the secondary electrolysis unit 300, the cation exchange membrane 240 is also sandwiched between the anode 322 and the cathode 332 in the electrolytic cell 210 with substantially no gap.

By configuring the cation exchange membrane 240 in this manner, the electrolytic cell 210 becomes a zero-gap type electrolytic cell.

[0064]

The primary anode solution AS1 delivered from the anode solution reservoir 250 of the primary electrolysis unit 200 is introduced into the anode solution reservoir 350 via the AS1 delivery pipe 256a.

As described above, the primary anolyte solution AS1, which contains chloric acid as its main component, contains sodium ions and hydrochloric acid.

[0065]

The anode solution reservoir 350 is connected to the anode tank 220 by pipes 350b and 350c.

The pipe 350b is a pipe that connects the lower side wall of the anode tank 220 and the lower side wall of the anode solution reservoir 350, and the pipe 350c is a pipe that connects the top surface of the anode tank 220 and the side wall of the anode solution reservoir 350.

[0066]

Here, the flow of the primary anolyte solution AS1 and the secondary anolyte solution AS2 will be described.

The primary anolyte AS1 introduced into the anolyte reservoir 350 is supplied to the anode tank 220 through a pipe 350b.

Then, by applying a voltage to the anode 322 and the cathode 332 using the DC stabilized power supply 260, the chloric acid in the primary anolyte solution AS1 is oxidized in the anolyte tank 220 to produce a secondary anolyte solution AS2.

The produced secondary anolyte solution AS2 is led back to the anolyte solution reservoir 350 via the pipe 350c.

Thereafter, the secondary anolyte solution AS2 repeats the above circulation.

[0067]

Furthermore, an exhaust pipe 350e is provided on the top surface of the anode solution reservoir 350 for exhausting oxygen and ozone generated at the anode 322 to the outside as the electrolytic oxidation progresses.

[0068]

Furthermore, the anode solution reservoir 350 communicates with a reaction tank 490 (described later) through an AS2 delivery pipe 356a.

The AS2 delivery pipe 356a is connected to the lower side wall of the anode solution reservoir 350, opposite the lower side wall to which the anode tank 220 is connected.

[0069]

By using a DC stabilized power supply 260, a voltage is applied to the anode 322 and the cathode 332 when the anode tank 220 contains the primary anode solution AS1 or the secondary anode solution AS2 and the cathode tank 230 contains H_2O or the cathode solution CS.

[0070]

As a result, the reactions shown in the following reaction formulas (10) to (12) proceed at the anode 322.

$HClO_3 + H_2O \rightarrow HClO_4 + 2H^+ + 2e^-$ ... Reaction formula (10) $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ ... Reaction formula (11) $3H_2O \rightarrow O_3 + 6H^+ + 6e^-$ ⋯Reaction formula (12)

[0071]

In this way, by applying a voltage to the anode 322 and the cathode 332 using the DC stabilized power supply 260, the reactions shown in the above reaction formulas (10) to (12) proceed in the anode tank 220.

This synthesizes perchloric acid.

As by-products, oxygen gas and ozone gas may be generated.

[0072]

The sodium ions contained in the secondary anolyte solution AS2 pass through the cation exchange membrane 240 due to the potential difference between the anode 322 and the cathode 332 and move from the anode chamber 220 to the cathode chamber 230.

As a result, in the cathode 332, the reactions shown in the above reaction formulas (8) and (9) proceed, similarly to the cathode 232 in the primary electrolysis unit 200.

[0073]

The oxygen gas and ozone gas that can be generated in the anode tank 220 are led to the anode solution reservoir 350 through a pipe 350c.

The oxygen gas and ozone gas are then sequentially exhausted to the outside through a pipe 350 e provided on the top surface of the anode solution reservoir 350 .

Therefore, similarly to the above-described anode solution reservoir 250, the secondary anode solution AS2 is sequentially introduced from the lower part of the anode tank 220 through the pipe 350b from the anode solution reservoir 350.

In other words, the secondary anolyte AS2 can be circulated between the anode tank 220 and the anolyte reservoir 350 without using a driving mechanism such as a pump.

[0074]

In the anode tank 220, when the content of perchloric acid in the secondary anode solution AS2 reaches a predetermined target value, the valves 358a and 258b are switched from a closed state to an open state by a control device (not shown).

As a result, the secondary anolyte AS2 is delivered from the anolyte reservoir 350 to the reaction tank 490 via the AS2 delivery pipe 356a.

On the other hand, the catholyte solution CS is discharged from the catholyte solution reservoir 252 to the outside through the CS delivery pipe 256b.

The content of perchloric acid in the secondary anolyte solution AS2 is determined from the relationship between the conversion rate from chloric acid to perchloric acid relative to the electrolysis time and the power consumption, which is proportional to the electrolysis time.

[0075]

When the electrolysis time is determined so as to maximize the rate of perchloric acid production relative to the power consumption, the chloric acid in the secondary anolyte AS2 cannot be completely converted to perchloric acid.

Furthermore, the sodium ions contained in the secondary anolyte solution AS2 do not completely migrate to the catholyte solution CS.

Generally, the secondary anolyte solution AS after the secondary electrolysis step contains several to 10% sodium ions.

Therefore, a treatment for reducing the sodium ion concentration contained in the secondary anolyte solution AS2 after the secondary electrolysis step is carried out in the reaction tank 490.

The basic compound introduction section 400, the carbon dioxide introduction section 450, the reaction tank 490, and the crystallization tank 492, which are characteristic of this embodiment, will be described below with reference to FIG.

[0076]

(Basic Compound Introducer 400, Carbon Dioxide Introducer 450, Reaction Tank 490, Crystallization Tank 492) Referring back to FIG. 1 , the basic compound introducer 400 includes a basic compound storage unit 410 for storing a basic compound, a valve 420, and an inlet pipe 422.

[0077]

The basic compound storage section 410 is in communication with the reaction vessel 490 via a valve 420 and an inlet pipe 422 .

The basic compound storage unit 410 stores carbonate, hydroxide, or ammonia.

Specifically, the basic compound storage unit 410 stores a compound selected from ammonium carbonate, lithium carbonate, potassium carbonate, lithium hydroxide, potassium hydroxide, aqueous ammonia, or ammonia.

[0078]

The basic compound stored in the basic compound storage unit 410, that is, the basic compound introduced into the reaction tank 490, may be selected depending on the target perchlorate.

For example, if the target perchlorate is ammonium perchlorate, ammonia or aqueous ammonia should be selected, and if the target perchlorate is potassium perchlorate, potassium carbonate or potassium hydroxide should be selected.

Here, an example in which ammonia gas is stored in the basic compound storage unit 410 will be described.

[0079]

The carbon dioxide introduction section 450 includes a carbon dioxide storage section 460 that stores carbon dioxide, a valve 470 , and an introduction pipe 472 .

The carbon dioxide storage section 460 is in communication with the reaction vessel 490 through a valve 470 and an inlet pipe 472 .

Furthermore, the carbon dioxide storage section 460 stores carbon dioxide (carbon dioxide gas).

[0080]

The secondary anode solution AS2 is introduced into the reaction tank 490 through the AS2 delivery pipe 356a, and ammonia gas is introduced from the basic compound storage unit 410 through a valve 420 and an introduction pipe 422.

Here, ammonia gas is introduced from the basic compound storage unit 410 into the reaction tank 490 until the pH of the secondary anolyte solution AS2 exceeds 7.0, preferably 12.0 or higher.

[0081]

As a result, the reactions shown in the following reaction formulas (13) and (14) proceed, and ammonium perchlorate is produced together with aqueous ammonia.

NH NER98 + H NER99 O → NH NER100 NER101 + OH NER102 ...Reaction formula (13) ClO NER103 NER104 + NH NER105 NER106 → NH NER107 ClO NER108 ...Reaction formula (14)

[0082]

Next, carbon dioxide is introduced into the reaction tank 490 from the carbon dioxide storage unit 460 through the valve 470 and the introduction pipe 472 .

As a result, the equilibrium reactions shown in the following reaction formulas (15) and (16) proceed in the reaction vessel 490.

As described above, when carbon dioxide is introduced into the secondary anode solution AS2 by the basic compound introducing unit 400 while the pH of the secondary anode solution AS2 is set to a value exceeding 7.0, that is, while the solution is made alkaline, the reaction proceeds from the left side to the right side of the above reaction formula (15), and hydrogen carbonate ions (HCO _３ [−]) and carbonate ions (CO _３ ^{２−}) are generated.

[0083]

Then, the reaction shown in the following reaction formula (17) or reaction formula (18) proceeds, producing sodium hydrogen carbonate (NaHCO 3 —NER115_) or sodium carbonate (Na 3 —NER116_ CO 3 —NER117_).

HCO 3 NER118 NER119 + Na NER120 → NaHCO 3 NER121 ...Reaction formula (17) CO 3 NER122 NER123 + 2Na NER124 → Na NER125 CO 3 NER126 ...Reaction formula (18) Furthermore, in addition to the reactions shown in the above reaction formulas (15) to (18), the reactions shown in the following reaction formulas (19) and (20) proceed, producing ammonium hydrogen carbonate (NH 3 NER127 HCO 3 NER128) or ammonium carbonate ((NH 3 NER129) NER130 CO 3 NER131).

HCO 3 NER132 NER133 + NH 3 NER134 NER135 → NH 3 NER136 HCO 3 NER137 ...Reaction equation (19) CO 3 NER138 NER139 + 2NH 3 NER140 NER141 → (NH 3 NER142) NER143 CO 3 NER144 ...Reaction equation (20) Here, the solubility of sodium bicarbonate and sodium carbonate in aqueous solution decreases as the pH increases.

Therefore, it is advisable to introduce ammonia into the secondary anolyte solution AS2 to such an extent that the sodium ions remaining in the secondary anolyte solution AS2 can be removed as a precipitate of sodium bicarbonate or sodium carbonate.

[0084]

In this manner, by adding a basic compound to the reaction tank 490 together with the secondary anode solution AS2 to adjust the pH of the secondary anode solution AS2 to a value above 7.0, preferably a value sufficiently above 12.0, and then introducing carbon dioxide, the sodium ions contained in the secondary anode solution AS2 are removed as a precipitate of sodium bicarbonate or sodium carbonate.

This makes it possible to significantly reduce the concentration of sodium ions in the aqueous solution contained in the reaction tank 490 and improve the purity of the target perchlorate.

[0085]

The crystallization tank 492 is connected to the reaction tank 490 via a valve 490a and an inlet pipe 490b.

The precipitates produced by the reactions represented by the above reaction formulas (17) and (18) are removed by filtration, and then the solution is evaporated and concentrated. An aqueous solution containing ammonium perchlorate, ammonium hydrogen carbonate, and ammonium carbonate (hereinafter referred to as the post-reaction aqueous solution) is introduced from the reaction tank 490 through a valve 490a and an inlet pipe 490b into a crystallization tank 492.

[0086]

In the crystallization tank 492, the concentrated post-reaction aqueous solution is cooled to crystallize ammonium perchlorate, ammonium hydrogen carbonate, and ammonium carbonate (cooling crystallization method).

The crystallized ammonium perchlorate, ammonium bicarbonate, and ammonium carbonate are then subjected to dehydration and drying treatments.

In the drying treatment, when the mixture is heated to a temperature at which ammonium perchlorate does not decompose and at which ammonium hydrogen carbonate and ammonium carbonate decompose (for example, about 80° C.), the reactions shown in the following reaction formulas (21) and (22) proceed.

NH 3 HCO 3 NER 146 → CO 3 NER 147 + NH 3 NER 148 + H 3 NER 149 O ...Reaction formula (21) (NH 3 NER 150) NER 151 CO 3 NER 152 → CO 3 NER 153 + 2NH 3 NER 154 + H 3 NER 155 O ... Reaction formula (22) Therefore, by adjusting the treatment temperature in the drying step, it is possible to remove the impurities, ammonium bicarbonate and ammonium carbonate.

[0087]

Finally, the ammonium perchlorate crystals are classified to make the particle size of the ammonium perchlorate crystals uniform.

[0088]

As described above, according to the perchlorate manufacturing apparatus 100 of this embodiment, a basic compound is added to the anolyte solution (secondary anolyte solution AS2) containing perchloric acid, which is generated by electrolytic oxidation using an aqueous solution containing sodium ions, to adjust the pH of the anolyte solution to a value greater than 7.0.

Then, by further introducing carbon dioxide into the anode solution whose pH has exceeded 7.0, the sodium ions contained in the anode solution are precipitated as sodium bicarbonate or sodium carbonate, thereby removing the sodium ions from the anode solution.

This makes it possible to significantly reduce the content of sodium salts as impurities, and improve the purity of the target product, ammonium perchlorate.

[0089]

(Method for Producing Perchlorate) Next, a method for producing perchlorate using the above-described apparatus 100 for producing perchlorate will be described.

FIG. 5 is a flowchart illustrating the process flow of the method for producing perchlorate according to this embodiment, and FIG. 6 is an explanatory diagram illustrating the state of the valves in each step of the method for producing perchlorate.

In the method for producing perchlorate in this embodiment, when a stop command is given by the user, the process currently being performed is stopped.

In addition, in the method for producing perchlorate, the sodium chloride aqueous solution and H_2O may be introduced into the primary electrolysis unit 200 after all of the following processes (steps, treatments) have been completed, or the sodium chloride aqueous solution and H_2O may be introduced into the primary electrolysis unit 200 sequentially, thereby carrying out each process in parallel and continuously.

[0090]

First, the control device (not shown) closes the valves 102, 104, 106, 254a, 254b, 258a, 258b, 358a, 420, 470, and 490a.

[0091]

When the control device opens the valve 102, the sodium chloride aqueous solution is stored in the anode tank 220 and the anode solution reservoir 250 of the primary electrolysis unit 200 (S500).

Furthermore, when the control device opens the valve 254a, H ₂ O is stored in the cathode tank 230 and the cathode solution reservoir 252 (S502).

Next, the control device closes the valves 102 and 254a, and applies a voltage to the anode 222 and the cathode 232 of the primary electrolysis unit 200 using the DC regulated power supply 260 (S504).

As a result, electrolysis begins in the primary electrolysis unit 200, and the oxidation reactions shown in the above reaction formulas (1) to (7) proceed in the anode tank 220.

Furthermore, in the cathode chamber 230, the reduction reactions shown in the above reaction formulas (8) and (9) proceed.

[0092]

Then, it is determined whether or not the chlorous acid in the primary anolyte solution AS1 shown in reaction formula (7) has been converted to chloric acid (S506).

If chlorous acid has not been converted to chloric acid (NO in S506), the application of voltage to the electrodes (anode 222 and cathode 232) using the DC stabilized power supply 260 is maintained.

[0093]

On the other hand, when the chlorous acid in the primary anode solution AS1 is converted to chloric acid (YES in S506), the application of voltage to the anode 222 and the cathode 232 using the DC regulated power supply 260 is stopped, and the primary electrolysis in the primary electrolysis unit 200 is terminated (S508).

[0094]

Next, the control device opens the valve 258a to introduce the primary anolyte AS1 produced in the primary electrolysis unit 200 into the anolyte solution reservoir 350 (anode tank 220) of the secondary electrolysis unit 300.

The control device also opens the valve 254b to introduce H_2O into the cathode solution reservoir 252 (cathode tank 230) of the secondary electrolysis unit 300 (S510).

[0095]

The control device closes the valves 258a and 254b, and applies a voltage to the anode 322 and the cathode 332 of the secondary electrolysis unit 300 using the DC regulated power supply 260 (S512).

As a result, electrolysis begins in the secondary electrolysis unit 300, and the oxidation reactions of the above reaction formulas (10) to (12) proceed in the anode tank 220.

Furthermore, in the cathode chamber 230, the reduction reactions of the above reaction formulas (8) and (9) proceed.

[0096]

It is determined whether or not the electrolysis time determined from the relationship between the conversion rate from chloric acid to perchloric acid relative to the electrolysis time and the power consumption proportional to the electrolysis time has elapsed (S514).

If the determined electrolysis time has not elapsed (NO in S514), the application of voltage to the electrodes (anode 222 and cathode 232) using the DC stabilized power supply 260 is maintained.

[0097]

On the other hand, if the determined electrolysis time has elapsed (YES in S514), the application of voltage to the anode 322 and the cathode 332 using the DC regulated power supply 260 is stopped, and the secondary electrolysis in the secondary electrolysis unit 300 is terminated (S516).

[0098]

Subsequently, the control device opens the valve 358 a to deliver the secondary anolyte AS2 produced in the secondary electrolysis unit 300 to the reaction tank 490.

The control device also opens the valve 258b to discharge the catholyte CS produced in the cathode tank 230 of the primary electrolysis unit 200 and the cathode tank 230 of the secondary electrolysis unit 300 to the outside (S518).

[0099]

The control device closes valve 358a and opens valve 420 in order to reduce the solubility of sodium bicarbonate and sodium carbonate, thereby introducing ammonia gas from basic compound storage unit 410 into reaction tank 490 until the pH of the secondary anode solution AS2 exceeds 7.0.

When the pH of the secondary anolyte solution AS2 exceeds 7.0, the valve 420 is closed (S520).

As a result, the reactions shown in the above reaction formulas (13) and (14) proceed in the reaction tank 490 to produce an aqueous solution containing ammonium perchlorate.

[0100]

The controller then causes valve 470 to open.

Then, carbon dioxide is introduced from the carbon dioxide storage unit 460 into the reaction tank 490, thereby causing the reactions shown in reaction formulas (15) to (20) to proceed (S522).

Then, the precipitate of sodium bicarbonate or sodium carbonate produced by the reactions shown in reaction formulas (17) and (18) is removed by filtration, and the resulting solution is taken out of the reaction tank 490 with the valve 104 in an open state.

Next, after the valve 104 is closed, the aqueous solution containing sodium bicarbonate or ammonium perchlorate from which the sodium carbonate precipitate has been removed is evaporated and concentrated (S524).

[0101]

The control device opens the valve 490a and introduces the aqueous solution containing ammonium perchlorate, ammonium bicarbonate, and ammonium carbonate (post-reaction aqueous solution) concentrated in the evaporation/concentration step (S524) from the reaction tank 490 into the crystallization tank 492 (S526).

The controller then opens valve 490a.

Subsequently, in the crystallization tank 492, the post-reaction aqueous solution is cooled to crystallize ammonium perchlorate, ammonium hydrogen carbonate, and ammonium carbonate.

[0102]

The control device then opens the valve 106, removes the crystallized ammonium perchlorate, ammonium bicarbonate, and ammonium carbonate, and subjects them to a dehydration treatment and further a drying treatment.

In such a drying treatment, when the mixture is heated to about 80° C., the reactions shown in the above reaction formulas (21) and (22) proceed, and ammonium hydrogen carbonate and ammonium carbonate are decomposed.

Subsequently, classification is carried out to make the particle size of the ammonium perchlorate crystals uniform (S528).

[0103]

The control device then closes the valves 106, 258b, and 470, thereby ending the perchloric acid production method.

[0104]

As described above, in the method for producing a perchlorate salt, a basic compound is added to the anolyte (secondary anolyte AS2) containing perchloric acid produced by electrolytic oxidation to adjust the pH of the anolyte to a value above 7.0, and carbon dioxide is then introduced.

As a result, sodium ions contained in the anolyte solution are precipitated as sodium bicarbonate or sodium carbonate, and the sodium ions can be removed from the anolyte solution.

[0105]

Although the preferred embodiments of the present invention have been described above with reference to the accompanying drawings, it goes without saying that the present invention is not limited to these embodiments.

It is clear that a person skilled in the art can think of various modifications or alterations within the scope of the claims, and it is understood that these also naturally fall within the technical scope of the present invention.

[0106]

For example, in the above-described embodiment, a sodium chloride aqueous solution has been described as an example of the solution contained in the anode tank 220 of the primary electrolysis unit 200.

However, there are no limitations on the raw material or the target substance as long as the solution can produce chloric acid by electrolytic oxidation.

For example, chlorides of other alkali metals such as potassium chloride (KCl) and lithium chloride (LiCl) can also be used as raw materials.

Furthermore, the aqueous solution is not limited to an aqueous solution of chlorides, but may be an aqueous solution containing at least one ion selected from the group consisting of hypochlorite ions, chlorite ions, and chlorate ions, and alkali metal ions.

[0107]

In the above-described embodiment, the electrolytic cell 210 is a zero-gap electrolytic cell.

However, the electrolytic cell may be one in which the cation exchange membrane 240 and the anodes 222 and 322 are separated from each other, and the cation exchange membrane 240 and the cathodes 232 and 332 are separated from each other.

[0108]

Furthermore, in the above-described embodiment, an example has been described in which the primary electrolysis and secondary electrolysis steps are carried out using two separate electrolytic baths.

However, there is no limitation on the electrolytic cell used for electrolysis.

For example, perchloric acid may be produced in one electrolytic cell.

Moreover, three or more electrolytic cells may be used to generate perchloric acid.

[0109]

A heating unit for heating the primary anolyte AS1 or the secondary anolyte AS2 may be provided below the anolyte reservoirs 250 and 350.

This can improve the production efficiency of the product produced on the surface of the anodes 222 and 322 .

In this case, it is advisable to provide a temperature measuring unit on the side wall of the anode tank 220 to measure the water temperature of the primary anode solution AS1 or the secondary anode solution AS2.

Then, based on the temperature measured by the temperature measurement unit, the output of the heating unit can be controlled so that the primary anode solution AS1 or the secondary anode solution AS2 contained in the anode tank 220 is maintained at a predetermined temperature that efficiently produces products on the surfaces of the anodes 222, 322.

[0110]

Similarly, a heating unit for heating the catholyte CS may be provided below the catholyte reservoir 252 .

As a result, the production efficiency of the product produced on the surface of the cathodes 232 and 332 can be improved.

In this case as well, it is advisable to provide a temperature measuring unit on the side wall of the cathode tank 230 to measure the temperature of the cathode solution CS.

Then, based on the temperature measured by the temperature measurement unit, the output of the heating unit can be controlled so that the cathode solution CS contained in the cathode tank 230 maintains a predetermined temperature that efficiently produces products on the surfaces of the cathodes 232, 332.

[0111]

Furthermore, valves and pumps may be provided at positions other than those shown in the perchlorate manufacturing apparatus 100.

[0112]

The steps of the method for producing perchlorate in this specification do not necessarily have to be performed in chronological order according to the order shown in the flowchart, and may include parallel or subroutine processing.

[0113]

The present invention relates to an apparatus for producing perchlorate and a method for producing perchlorate.

[0114]

DESCRIPTION OF SYMBOLS 100 Perchlorate manufacturing apparatus 200 Primary electrolysis unit 210 Electrolytic cell 220 Anode cell 222, 322 Anode 230 Cathode cell 232, 332 Cathode 240 Cation exchange membrane 260 DC stabilized power supply 300 Secondary electrolysis unit 400 Basic compound introduction section 410 Basic compound storage section 450 Carbon dioxide introduction section 460 Carbon dioxide storage section 490

Reaction tank 492 Crystallization tank
