

METHOD FOR PRODUCING HIGH-PURITY MAGNESIUM CARBONATE USING SEAWATER DESALINATION BRINE

TECHNICAL FIELD

[0001] The present invention relates to a technology for producing magnesium carbonate from brine, which is discharged as a by-product of seawater desalination and in which magnesium and sodium are concentrated, and for treating the sodium.

[0002]

BACKGROUND

[0003] In a seawater desalination plant, seawater is produced into fresh water by a reverse osmosis method or the like, wherein approximately 50% of the seawater is converted into fresh water and the remaining 50% has metal cations concentrated at a much higher concentration than the original seawater. That is, the concentrated water contains cations at levels of sodium 18,298 mg/L, magnesium 2,715 mg/L, and calcium 774 mg/L. Since directly discharging into the ocean the concentrated water, in which metals are dissolved at such high concentrations, may affect the ecosystem, seawater is drawn in and mixed with the concentrated water to dilute the same before being discharged. However, since environmental issues regarding the discharge of the concentrated water have recently been raised in Europe and elsewhere, fundamental countermeasures are required.

[0004] Meanwhile, since the metals in the concentrated water are concentrated at high concentrations, schemes for recycling them from the viewpoint of a raw material rather than waste have been proposed. Conventionally, methods of fixing carbon dioxide by reacting calcium and magnesium with carbon dioxide have mainly been proposed, but

these had carbon reduction as their main purpose and had limitations in terms of recycling as an industrial raw material.

[0005]

DETAILED DESCRIPTION OF THE INVENTION

TECHNICAL PROBLEM

[0006] An object of the present invention, which is intended to solve the above-described problems, is to provide a method for recycling magnesium in the concentrated water as a high-quality industrial raw material and simultaneously providing a method capable of removing carbon dioxide.

[0007] Meanwhile, other objects of the present invention that are not explicitly specified shall be additionally considered within a range that can be easily inferred from the following detailed description and effects thereof.

[0008]

TECHNICAL SOLUTION

[0009] In order to solve the problem described above, the following solving means is proposed.

[0010] The method for producing magnesium carbonate using SEAWATER DESALINATION BRINE according to the present invention for achieving the above object is characterized by comprising: (A) a step of continuously supplying the seawater desalination brine and an alkaline solution to a first reactor and reacting them, thereby

forming solid-state magnesium hydroxide; (B) a step of continuously separating and discharging the solid-state magnesium hydroxide from the concentrated water continuously supplied from the first reactor to a first solid-liquid separator; (C) a step of transferring the concentrated water discharged from the first solid-liquid separator to a second reactor and introducing a polymer hydrogel to bind and remove residual magnesium and calcium in the concentrated water; (D) a step of mixing water with the magnesium hydroxide discharged from the first solid-liquid separator to form a mixed liquid, and supplying the mixed liquid together with carbon dioxide to a third reactor to precipitate magnesium carbonate; (E) a step of supplying the mixed liquid from the third reactor to a third solid-liquid separator to separate and discharge the magnesium carbonate; and (F) a step of producing sodium hydroxide, hydrogen, and chlorine, through a chlor-alkali process, with respect to the concentrated water discharged from the second reactor, to reduce a concentration of sodium in the concentrated water.

[0011] Meanwhile, another method for producing magnesium carbonate using seawater desalination brine according to the present invention is characterized by utilizing a hydrogel. That is, the present invention is characterized by comprising: (A) a step of continuously supplying seawater desalination brine and an alkaline solution to a first reactor and reacting them, thereby forming solid-state magnesium hydroxide; (B) a step of continuously separating and discharging the solid-state magnesium hydroxide from the concentrated water continuously supplied from the first reactor to a first solid-liquid separator; (C) a step of supplying, together with the concentrated water discharged from the first solid-liquid separator, an alkaline solution and carbon dioxide to a second reactor, thereby forming calcium carbonate in a solid state; (D) a step of separating the calcium

carbonate from the concentrated water supplied from the second reactor to a second solid-liquid separator; (E) a step of mixing water with the magnesium hydroxide discharged from the first solid-liquid separator to form a mixed liquid, and supplying the mixed liquid together with carbon dioxide to a third reactor to precipitate magnesium carbonate; (F) a step of supplying the mixed liquid from the third reactor to a third solid-liquid separator to separate and discharge the magnesium carbonate; and (G) a step of producing sodium hydroxide, hydrogen, and chlorine, through a chlor-alkali process, with respect to the concentrated water discharged in a liquid phase from the second solid-liquid separator, to reduce a concentration of sodium in the concentrated water.

[0012] In the embodiments of the above two inventions, the following technical limitations and additions are possible.

[0013] In an example of the above present inventions, the carbon dioxide supplied to the third reactor is in the form of microbubbles having a particle diameter of 50 micrometers or less, and the microbubbles may be supplied while being pressurized to 5 bar or less.

[0014] Also, in an example of the present inventions, the alkaline solution supplied to the first reactor is supplied at a ratio of 1.8 to 2.2 times relative to a number of moles (mol) of magnesium in the concentrated water.

[0015] Also, in an example of the present inventions, the first reactor has an inlet formed on one side and an outlet formed on the other side, and includes a tubular stirring section in which a plurality of protrusions are formed protruding on an inner peripheral surface so as to generate a turbulent flow in the concentrated water. In particular, the first

reactor includes a reaction section disposed at a rear end of the tubular stirring section, in which the magnesium hydroxide is formed. Also, it is preferable to further include a spray nozzle that is inserted into an inside of the tubular stirring section and supplies the alkaline solution along a flow direction of the concentrated water.

[0016] In an example of the present inventions, the first solid-liquid separator comprises: a chamber having a shape in which a diameter increases from an upper side toward a lower side and then decreases again, the chamber being provided with a space portion therein for mutually separating solid and liquid of the concentrated water, an inlet through which the concentrated water flows in being formed at a lower portion thereof, a discharge hole being formed at an upper central portion thereof, and a plurality of slits in an elongated hole shape being formed along a circumferential direction in a region of largest diameter; a shutter installed in the space portion inside the chamber so as to be vertically movable between a first position closing the slits and a second position opening the slits; and a cover portion in which a flow path for guiding the solid discharged through the slits of the chamber is formed; wherein, while the shutter rotates with the slits closed, the liquid in the concentrated water is continuously discharged through the discharge hole, and the solid in the concentrated water moves to a portion of largest diameter in the chamber and is discharged through the slits when the shutter is spaced downward.

[0017] In an example of the present inventions, the mixed liquid is continuously supplied to and discharged from the third reactor,

[0018]

$$V_{gas}(L/sec) = \frac{22.4 \cdot V_w(L/sec) \cdot C_{mg}(mol/L) \cdot A}{T_{co2} \cdot P_{co2} \cdot z}$$

... Equation (1)

[0019] (where V_{gas} is a gas injection amount per unit time, V_w is a mixed liquid injection amount per unit time, C_{mg} is a molar concentration of magnesium in the mixed liquid, A is a volume correction coefficient of carbon dioxide, T_{co2} is a conversion rate (0.01 to 1) at which the carbon dioxide participates in a carbonation reaction, P_{co2} is a concentration of carbon dioxide in flue gas (0.01 to 1 as a volume ratio), z is a target mineral coefficient (0.5, 0.8, 1) that determines a specific form of the magnesium carbonate to be produced, and 22.4 is a volume (L) of 1 mole of an ideal gas).

[0020] An injection amount per unit time of the gas containing carbon dioxide supplied to the third reactor may be determined by Equation (1) above

[0021] In an example of the present inventions, the water mixed with the magnesium hydroxide is fresh water, and it is preferable that the mixed liquid discharged from the third solid-liquid separator is supplied again to the third reactor to be circulated.

[0022] In an example of the present inventions, sodium hydroxide and chlorine generated in the chlor-alkali process may be mixed to form sodium hypochlorite.

[0023] In an example of the present invention, when the concentration of the sodium hydroxide produced in the chlor-alkali process is 10 mass% or more, it is possible

to additionally produce sodium bicarbonate (NaHCO_3) or sodium carbonate (Na_2CO_3) by injecting carbon dioxide into the sodium hydroxide.

[0024]

ADVANTAGEOUS EFFECTS

[0025] In the present invention, an alkaline solution is supplied to concentrated water generated in a seawater desalination plant to form magnesium hydroxide, and the magnesium hydroxide is then reacted with carbon dioxide to produce high-quality magnesium carbonate that is usable as an industrial raw material, and during this process, carbon dioxide, which is a greenhouse gas, is removed. In particular, since the above process is carried out continuously, mass production of the magnesium carbonate is possible.

[0026] In addition, the calcium in the concentrated water may be adsorbed onto a hydrogel to form a hydrogel composition having an ability to remove carbon dioxide, thereby ultimately increasing a carbon dioxide treatment amount.

[0027] With respect to the sodium-rich concentrated water from which the magnesium and calcium have been removed, sodium hydroxide and chlorine gas are produced and recycled through a chlor-alkali process, thereby forming a circulating process. In addition, since the sodium in the concentrated water is consumed as the sodium hydroxide is formed, there is an advantage that the TDS standard can be met when the concentrated water is disposed of.

[0028] Meanwhile, it is added that, even for effects not explicitly mentioned herein, the effects described in the following specification and the tentative effects thereof, which

are expected by the technical features of the present invention, are to be treated as if described in the specification of the present invention.

[0029]

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] FIG. 1 is a schematic flowchart of a method for producing magnesium carbonate using seawater desalination brine according to a first embodiment of the present invention.

[0031] FIG. 2 is a schematic view of a continuous-type reactor.

[0032] FIG. 3 is a schematic cross-sectional view taken along line a-a of FIG. 2.

[0033] FIG. 4 is a schematic view of a first solid-liquid separator.

[0034] FIG. 5 is a view for explaining how calcium is substituted in sodium alginate to crosslink the sodium alginate.

[0035] FIG. 6 is a schematic flowchart of a method for producing magnesium carbonate using seawater desalination brine according to a second embodiment of the present invention.

[0036] * It is to be noted that the accompanying drawings are illustrated only for reference for understanding the technical concept of the present invention, and the scope of rights of the present invention is not limited thereby.

[0037]

DETAILED DESCRIPTION OF EMBODIMENTS

[0038] In describing the present invention, when it is determined that a related publicly known function may unnecessarily obscure the gist of the present invention as a matter obvious to a person skilled in the art, a detailed description thereof will be omitted.

[0039] Hereinafter, with reference to the accompanying drawings, the method for producing magnesium carbonate using seawater desalination brine according to the first embodiment of the present invention (hereinafter referred to as the "method for producing magnesium carbonate") will be described in more detail.

[0040] FIG. 1 is a schematic flowchart of the method for producing magnesium carbonate using seawater desalination brine according to the first embodiment of the present invention, FIG. 2 is a schematic view of a continuous-type reactor, FIG. 3 is a schematic cross-sectional view taken along line a-a of FIG. 2, and FIG. 4 is a schematic view of a first solid-liquid separator.

[0041] The method for producing magnesium carbonate according to the first embodiment of the present invention is for producing magnesium carbonate by reacting concentrated water generated as a by-product in a seawater desalination plant with carbon dioxide. In the present invention, although there is also an object of removing carbon dioxide, a more important object is to produce high-quality magnesium carbonate. Furthermore, the present invention seeks to implement a process capable of commercial mass production through a continuous process.

[0042] In the present specification, "carbon dioxide" refers to flue gas generated in the process of generating power consumed by the seawater desalination plant, and also includes flue gas generated at other industrial sites. Although flue gas of course contains various components and carbon dioxide is included in an amount of approximately 15%, it is expressed as carbon dioxide gas (gas phase) for convenience of description. Although the present invention also does not exclude using 100% carbon dioxide gas through means such as separately capturing only carbon dioxide from the flue gas, it is preferable to directly use the flue gas in consideration of process economy and carbonation efficiency.

[0043] In the concentrated water used as a starting material in the present invention, metal cations are abundantly dissolved. For example, the concentrated water discharged from a single domestic desalination plant site contains sodium at 18,298 mg/L, magnesium at 2,715 mg/L, calcium at 774 mg/L, and potassium at 711 mg/L, and additionally lithium, strontium, and the like, although not at high concentrations, are also dissolved therein.

[0044] In the present example, an alkaline solution (NaOH in the present example) is first supplied to the concentrated water to raise the pH to a level of approximately 10.5, thereby producing magnesium in the concentrated water as solid-state magnesium hydroxide. In particular, the object of the present example is to implement a continuous process so that commercial mass production is possible. That is, in the present example, the process of mixing, stirring, and reacting the concentrated water and the alkaline solution, and the subsequent solid-liquid separation process of separating the magnesium hydroxide produced in a solid state, are all carried out continuously. In the conventional manner, the concentrated water and the alkaline solution were charged together into the reactor and stirred while being allowed to stand for a certain time to produce magnesium

hydroxide, and then the concentrated water in the reactor was transferred to a solid-liquid separator all at once. However, in the present example, the concentrated water passes through a first reactor and directly flows into a first solid-liquid separator. That is, the concentrated water is not allowed to stand within the first reactor but is continuously moved while the magnesium hydroxide is produced and discharged to the first solid-liquid separator.

[0045] To this end, the first reactor 10 is formed in an elongated tubular shape as shown in FIG. 2. The concentrated water flows in through one side of the first reactor 10 and is discharged through the other side. In addition, a sodium hydroxide solution is supplied into the first reactor. An important point is that the concentrated water and the sodium hydroxide must be uniformly mixed within a short time. Since the concentrated water is continuously moved without being allowed to stand at one location as in the conventional manner, it must be uniformly stirred with the sodium hydroxide solution within a short time. Accordingly, in the present example, a spray nozzle 17 is inserted into and coaxially disposed in a front portion of the tubular first reactor 10. The spray nozzle 17 supplies the alkaline solution along a flow direction of the concentrated water. In the present example, in particular, the spray nozzle is configured in a showerhead form to radially spray the alkaline solution so that the alkaline solution can be mixed throughout the concentrated water. Of course, in another example, the spray nozzle may not be inserted into the first reactor, but as in the present example, being inserted into and coaxially disposed inside the reactor can improve stirring efficiency.

[0046] In addition, a stirring section 12 in which protrusions 11 are formed on an inner peripheral surface is provided at a front portion of the tubular first reactor 10, and a

reaction section 13 without protrusions is provided at a rear portion. The protrusions 11 obstruct the flow of the concentrated water and form a turbulent flow, thereby providing the advantage that the mixing of the concentrated water with the alkaline solution is promoted. Of course, depending on the embodiment, protrusions may be formed on the inner peripheral surface over the entire length of the first reactor, or the first reactor may be formed only in a tubular shape without protrusions. However, as in the present example, when the stirring section is formed at the front portion, mixing efficiency increases, and when there are no protrusions at the rear portion, the magnesium hydroxide can be stably produced, which is effective.

[0047] Meanwhile, a supply amount of the alkaline solution is determined in proportion to a supply amount of the concentrated water. In the case of using a stationary-type reactor, the alkaline solution may be injected while continuously measuring the pH within the reactor using a pH sensor, but in a continuous-type reactor as in the present example, since the concentrated water continuously flows, it is not appropriate to control the pH using a sensor. Accordingly, the injection amount (injection rate) of the alkaline solution is determined in advance before the concentrated water is introduced into the first reactor, and is continuously supplied. In the present example, a sodium hydroxide solution is supplied at a ratio of 1.8 to 2.2 times relative to a number of moles (mol) of magnesium in the concentrated water. That is, when the supply amount of the concentrated water per unit time (e.g., 1 second, 1 minute) is determined, the number of moles of magnesium in the concentrated water can be known, and the sodium hydroxide solution is supplied such that the number of moles of sodium hydroxide is 1.8 to 2.2 times relative to the number of moles of magnesium. During the determined unit time, the concentrated water and the

alkaline solution are each supplied at a constant rate. When the number of moles is within the above-described range, the pH of the concentrated water may be formed to be approximately 10.5.

[0048] The concentrated water discharged from the first reactor is supplied to the first solid-liquid separator to separate the solid-state magnesium hydroxide therefrom. In the present example, the first solid-liquid separator also uses a continuous-type separator, such that the concentrated water is continuously supplied and the solid-state magnesium hydroxide is continuously separated. The configuration of the centrifugal separator used in the present example will be briefly described.

[0049] Referring to FIG. 4, the continuous-type centrifugal separator 50 used in the present example includes a chamber 20, a shutter 30, and a cover portion 40. The chamber 20 is coupled to a rotation shaft 21 and installed to be rotated. The chamber 20 includes an upper half portion 22, whose diameter gradually expands from an upper side toward a central portion to form a cone shape, and a lower half portion 23, which extends downward from the upper half portion 22 and whose diameter gradually decreases. Inside the chamber 20, a space portion 24 for mutually separating solid and liquid in the concentrate is formed. In addition, an inlet pipe 25 is inserted from an upper side of the chamber 20 to the space portion 24. The concentrated water flows into a lower side of the space portion 24 through an inlet opened at a lower end of the inlet pipe 25. On the upper side of the chamber 20, a discharge hole 26 through which the solid-liquid-separated liquid is discharged is formed. In addition, a slit 27 is formed at a boundary point between the upper half portion 22 and the lower half portion 23, that is, at a point of the largest diameter. The slit 27 is a passage through which the solid-state magnesium hydroxide separated from the concentrated water

is discharged. A plurality of slits 27 are arranged spaced apart from each other along a circumferential direction of the chamber 20. In addition, in the present example, the slits are formed in an elongated hole shape along the circumferential direction of the chamber so that the magnesium hydroxide is efficiently discharged while the chamber rotates.

[0050] The shutter 30 is installed in the space portion 24 to be vertically movable between a first position and a second position. When the shutter 30 is in the first position in which it is raised, the shutter blocks and seals the slit 27. On the other hand, in the second position in which the shutter is lowered, the slit 27 is opened. The shutter 30 is in the first position, which is a default position, and periodically opens the slit 27 briefly and then seals the slit again.

[0051] The cover portion 40 is disposed to surround a region of the chamber 20 having the largest diameter, that is, a point where the plurality of slits 27 are formed, and forms a circumferential flow path 41 into which the magnesium hydroxide discharged through the slits 27 of the chamber 20 flows. The flow path 41 is connected to a pump (not shown).

[0052] In addition, a plurality of disks 28 are stacked in the space portion 24, and a passage portion 29 is formed between the disks 28. The disks 28 are also formed in a conical shape corresponding to the upper half portion 22 of the chamber, such that the diameter increases from an upper side toward a lower side. As indicated by the arrows in FIG. 4, the disks 27 guide the liquid in the concentrate toward the central portion of the chamber.

[0053] In the continuous-type centrifugal separator having the above-described configuration, the chamber 20 is continuously rotated to mutually separate the liquid and solid in the concentrated water. That is, the concentrated water containing the magnesium hydroxide is continuously introduced through the inlet pipe 25, and the chamber 20 also continues to rotate. The magnesium hydroxide, which is in a solid state in the concentrated water, is pushed outward within the space portion 24 by centrifugal force and is gathered near a point of the largest diameter in the chamber, that is, near the slits 27. However, since the slits 27 are closed by the shutter 30, the magnesium hydroxide cannot be discharged. The liquid component, on the other hand, moves to the central portion of the chamber through the passage portions 29 between the plurality of disks 28, and is then continuously discharged through the discharge hole 26. The magnesium hydroxide gathered near the slits is, when the shutter 30 descends and temporarily opens the slits 27, passed through the slits 27 and discharged into the flow path 41. In this manner, the supply of the concentrated water, the solid-liquid separation in the concentrated water, and the discharge of the liquid component and the solid component are carried out continuously. However, even if the first solid-liquid separator is not in the above form, any form may be used as long as solid-liquid separation is possible continuously.

[0054] The concentrated water from which the solid-state magnesium hydroxide has been separated through the first solid-liquid separation is supplied to the second reactor. In the second reactor, a polymer hydrogel or a polymer resin is introduced into the concentrated water to bind and remove residual magnesium and calcium in the concentrated water.

[0055] In the present example, sodium alginate (SA, Sodium Alginate) is used as the polymer hydrogel. However, in addition thereto, as a synthetic polymer material, at least one selected from the group consisting of polyacrylic acid, polyacrylamide, kappa-carrageenan, karaya gum, amidated pectin, carboxymethyl cellulose, polytetrafluoroethylene, polyethylene, polyurethane, polyethylene glycol, and polyester may be used. As a natural polymer material, at least one selected from the group consisting of hyaluronic acid, heparin, dextran, collagen, albumin, gelatin, and chitosan may be used.

[0056] The polymer hydrogel becomes viscous as it dissolves in an alkaline solution, and since the concentrated water is supplied with a sodium hydroxide solution and is basic, the polymer hydrogel dissolves in the concentrated water. Then, as illustrated in FIG. 5, calcium or magnesium in the concentrated water substitutes for sodium sites in the dissolved sodium alginate, thereby performing a crosslinking role of mutually connecting the sodium alginate chains. Accordingly, the sodium alginate is converted into calcium alginate or magnesium alginate. As a plurality of alginate chains are connected and solidified by calcium or magnesium, a gel state is formed. The hydrogel material formed in this manner can remove carbon dioxide in the air. That is, the calcium or magnesium contained in the hydrogel material is combined with carbon dioxide in the air and converted into calcium carbonate or magnesium carbonate, and is removed.

[0057] Meanwhile, even in the case of polymer hydrogels other than sodium alginate, calcium and magnesium can cause the polymer chains to aggregate with each other through actions such as polymerization, bonding, and crosslinking, thereby effecting gelation. The expression earlier that the hydrogel binds and removes calcium and magnesium can be understood as collectively referring to the chemical reactions as

described above. For reference, it is added that, instead of introducing the hydrogel directly into the concentrated water, the hydrogel may be dissolved in a separate alkaline solution and the dissolved solution may then be introduced into the concentrated water.

[0058] Meanwhile, the magnesium hydroxide solid-liquid-separated in the first solid-liquid separator is mixed with water (fresh water) in a mixing tank to form a mixed liquid, and is then supplied to the third reactor. In another modified example, the magnesium hydroxide and the concentrated water discharged from the second solid-liquid separator may be mixed to form the mixed liquid, but in the first embodiment, fresh water is mixed to form the mixed liquid. Although using the concentrated water may be economical because fresh water is not used, since various ions are contained as impurities, this is not preferable in terms of improving the purity of the magnesium carbonate. Since the technical objective of the present embodiment is to produce high-purity, high-quality magnesium carbonate that does not contain impurities, it is advantageous to use fresh water that does not contain impurities to prepare the mixed liquid.

[0059] In addition, carbon dioxide is supplied to the third reactor, and the carbon dioxide and the magnesium react to produce magnesium carbonate, which then precipitates. In the present embodiment, the third reactor also uses a continuous-type reactor to which the mixed liquid is continuously supplied and from which the mixed liquid is continuously discharged. For example, a tubular reactor that is elongated in one direction and has an inlet formed on one side and an outlet formed on the other side may be used. The length of the continuous-type reactor may be adjusted such that a residence time sufficient for the carbon dioxide and the magnesium in the mixed liquid to react and form magnesium carbonate is ensured. In addition, in order to promote the formation of

magnesium carbonate, the carbon dioxide is pressurized to a pressure of 5 bar or less (4 to 5 bar) and injected after being made into a size having a particle diameter of 50 μm or less (1 to 50 μm), and preferably 10 μm or less. When the carbon dioxide is made into a micro size, the surface area of the carbon dioxide is widened so that the contact with the magnesium becomes more active, and thus the magnesium carbonate production efficiency is improved.

[0060] Meanwhile, in a continuous process, it is important to determine an injection amount of carbon dioxide per unit time in advance. In a continuous process, since the mixed liquid containing the magnesium continuously passes through, for example, the tubular reactor, the carbon dioxide must also be continuously injected. When a reaction was conventionally carried out in a stationary manner using a batch-type reactor, a pH sensor was used. That is, a method was used in which, when carbon dioxide is injected, the pH of the mixed liquid gradually decreases, and the injection of carbon dioxide is stopped when the pH reaches about 8 to 9. However, in a continuous-type process, it is difficult to apply such a method. Accordingly, the injection amount of carbon dioxide or the injection amount per unit time must be determined in advance and supplied at a constant rate to the third reactor. Accordingly, in the present invention, the following Equation (1) is used so as to determine the injection amount of carbon dioxide per unit time in advance in order to implement the continuous process.

[0061]

$$V_{gas}(L/sec) = \frac{22.4 \cdot V_w(L/sec) \cdot C_{mg}(mol/L) \cdot A}{T_{co2} \cdot P_{co2} \cdot z} \quad \dots \text{Equation (1)}$$

[0062] (where V_{gas} is a gas injection amount per unit time, V_w is a mixed liquid injection amount per unit time, C_{mg} is a molar concentration of magnesium in the mixed liquid, A is a volume correction coefficient of carbon dioxide, T_{co2} is a conversion rate (0.01 to 1) at which the carbon dioxide participates in a carbonation reaction, P_{co2} is a concentration of carbon dioxide in flue gas (0.01 to 1 as a volume ratio), z is a target mineral coefficient (0.5, 0.8, 1) that determines a specific form of the magnesium carbonate to be produced, and 22.4 is a volume (L) of 1 mole of an ideal gas).

[0063] Equation (1) above starts from Equation (2) below, and basically makes the number of moles of carbon dioxide supplied per unit time correspond equally to the number of moles of magnesium.

[0064]
$$\frac{V_{\text{gas}}(\text{L/sec}) \cdot P_{\text{co2}} \cdot z \cdot T_{\text{co2}}}{22.4 \cdot A} = V_w(\text{L/sec}) \cdot C_{\text{mg}}(\text{mol/L}) \quad \dots \text{Equation (2)}$$

[0065] Excluding A and z , the left side is the number of moles of carbon dioxide that flows in per unit time and participates in the carbonation reaction, and the right side is the number of moles of magnesium that flows in per unit time. The volume of carbon dioxide is obtained by multiplying the concentration of carbon dioxide in the flue gas (volume %, e.g., 0.15), and then dividing by 22.4 (L), the volume of 1 mole of carbon dioxide, to obtain the number of moles of carbon dioxide gas flowing in per unit time. In the case of the right side, multiplying the flow rate of the mixed liquid per unit time by the molar concentration (mol/L) of magnesium in the mixed liquid yields the number of moles of magnesium per unit time. However, since the volume of 1 mol of carbon dioxide gas

may differ from 22.4 L as for an ideal gas, correction is possible within a volume correction coefficient range of 0.85 to 1.15.

[0066] In the above equation, the value of z is related to a specific form of the magnesium carbonate. The value of z is determined according to the type of magnesium carbonate to be produced. For example, when a target mineral is artinite, $z=0.5$ is substituted to reduce the injection amount of carbon dioxide, and when the target mineral is hydromagnesite or dypingite, z is set to 0.8. In addition, when the target mineral is magnesite, barringtonite, nesquehonite, or lansfordite, $z=1$ is used. The above target mineral coefficients are derived from research results based on the ratio between magnesium and carbonate ions in each mineral. As described above, when the flow rate of the mixed liquid (containing magnesium) per unit time is known and the concentration of magnesium in the mixed liquid is known, the injection amount per unit time of the gas containing carbon dioxide may be determined in advance by Equation (1) above. The flow rate of the mixed liquid per unit time may be controlled by a pump. In addition, since the concentration of magnesium in the mixed liquid can be grasped in real time by installing a sensor, even when the inflow amount per unit time of the mixed liquid and the concentration of magnesium change in real time, the injection amount of carbon dioxide per unit time can be changed in real time.

[0067] For reference, when the magnesium carbonate production process is carried out not in a continuous manner but in a semi-batch manner, that is, the process may be carried out in units of a predetermined amount of the mixed liquid. In this case, the injection time of carbon dioxide in a batch-type third reactor may be determined by Equation (3)

below. Equation (3) below is also obtained by modifying Equation (1) above to suit a batch type.

[0068]
$$T_{gas}(\text{sec}) = \frac{Q_w(L) \cdot C_{mg}(\text{mol/L}) \cdot A \cdot 22.4}{V_{gas}(L/\text{sec}) \cdot P_{co2} \cdot z \cdot T_{co2}} \dots \text{Equation (3)}$$

[0069] In Equation (3) above, the left side is an injection time of flue gas, Q_w on the right side is a volume of one batch of the mixed liquid that flows into the third reactor for one reaction process, C_{mg} is a molar concentration of magnesium in the mixed liquid, A is a volume correction coefficient of carbon dioxide, V_{gas} is a flow rate of flue gas per unit time, P_{co2} is a concentration of carbon dioxide in flue gas (0.01 to 1 as a volume ratio), z is a target mineral coefficient that determines a specific form of the magnesium carbonate to be produced, T_{co2} is a conversion rate of carbon dioxide participating in the carbonation reaction, and 22.4 is a volume (L) of 1 mole of an ideal gas. For reference, Equation (3) above can also be used when producing calcium carbonate in a semi-batch manner by being modified in the same manner as Equation (1).

[0070] As described above, after the carbon dioxide and the magnesium have mutually reacted, the mixed liquid discharged from the third reactor is supplied to the third solid-liquid separator, and in the third solid-liquid separator, the solid-state magnesium carbonate is separated from the mixed liquid. In the present embodiment, the third solid-liquid separator may implement a continuous process by using a filter press. Since the mixed liquid from which the magnesium carbonate has been separated in the third solid-liquid separator is in a fresh-water state or in a state in which some residual magnesium

remains, it is transferred again to the mixing tank to be reused, thereby creating a circulating process.

[0071] Meanwhile, since the concentrated water discharged from the second reactor contains sodium at a high concentration, it is not preferable to discharge it as is into the ocean. Accordingly, in the present invention, the concentrated water is introduced into a chlor-alkali process to produce sodium hydroxide, hydrogen, and chlorine, thereby reducing the concentration of sodium in the concentrated water. In addition, the sodium hydroxide produced herein can be reused as the alkaline solution in the first reactor and the second reactor to achieve a circulating process.

[0072] The chlor-alkali process is mainly used for producing chlorine, and sodium hydroxide is produced as a by-product. Although the chlor-alkali process originally involves mixing salt with water to make brine and then performing electrolysis, since in the present invention the concentrated water itself contains sodium at a concentration of about 20,000 mg/L, the chlor-alkali process can be carried out by performing electrolysis on the concentrated water as it is. Through the chlor-alkali process, sodium hydroxide, hydrogen, and chlorine can each be recovered.

[0073] Although the sodium hydroxide generated in the chlor-alkali process is reused as the alkaline solution for adjusting the pH of the concentrated water, separately therefrom, it may also be mixed with chlorine gas to produce sodium hypochlorite. In addition, when the concentration of the sodium hydroxide produced in the chlor-alkali process is 10% (mass%) or more, carbon dioxide may be injected into the sodium

hydroxide to additionally produce sodium bicarbonate (NaHCO_3) or sodium carbonate (Na_2CO_3).

[0074] As described above, since the chlor-alkali process is a process of dissolving NaCl in water to form brine and then performing electrolysis, only monovalent ions are dissolved in the brine. However, in the case of using the desalination concentrated water as in the present invention, various ions are dissolved therein. Although the magnesium has been removed from the concentrated water as the magnesium hydroxide and the calcium has been removed using the hydrogel in the preceding processes, residual ions may remain. When the concentrated water containing divalent ions is utilized in the chlor-alkali process, there is a problem in that the electrolysis efficiency decreases. Accordingly, in the present invention, with respect to the concentrated water separated in the second reactor, divalent cations and monovalent cations may be mutually separated through electrodialysis, and then only the concentrated water containing the monovalent cations may be utilized in the chlor-alkali process.

[0075] Meanwhile, the second embodiment of the present invention is shown in FIG. 6.

[0076] Referring to FIG. 6, the second embodiment is completely the same as the first embodiment with respect to the process of producing magnesium carbonate by sequentially moving seawater desalination brine through a first reactor, a first solid-liquid separator, a mixing tank, a third reaction tank, and a third solid-liquid separation. The first reactor, the first solid-liquid separator, the mixing tank, the third reaction tank, the third solid-liquid separator, and the specific processes described in the first embodiment are used

identically in the second embodiment as well. Accordingly, the magnesium treatment process will be replaced with the description for the first embodiment.

[0077] The difference between the second embodiment and the first embodiment is the treatment process for the liquid component (concentrated water) after solid-liquid separation in the first solid-liquid separator. Although in the first embodiment a hydrogel was added to the concentrated water to remove divalent ions including calcium ions, in the second embodiment the calcium ions are reacted with carbon dioxide to form calcium carbonate.

[0078] Referring to the second embodiment shown in FIG. 6, the concentrated water from which the solid-state magnesium hydroxide has been separated through the first solid-liquid separator is supplied to a second reactor. In addition, an alkaline solution (e.g., a sodium hydroxide solution) is supplied together to the second reactor, and carbon dioxide is injected therein. In the second reactor, the calcium in the concentrated water reacts with the carbon dioxide to be produced into solid-state calcium carbonate. In the second embodiment, the second reactor also uses a continuous-type reactor, like the first reactor. However, since the main process of the present invention is the process of producing and separating the magnesium hydroxide and subsequently producing magnesium carbonate from the magnesium hydroxide, the calcium carbonate process, which is not the main process, may not be configured in a continuous-type but may be configured in a batch type in which the concentrated water is collected at predetermined time intervals and then treated. In the second embodiment, it is implemented as a continuous-type process, in which the concentrated water is continuously supplied to and discharged from the second reactor, and in this process, the alkaline solution is first supplied and stirred, and the carbon

dioxide is injected. Depending on the embodiment, the second reactor may be divided into two portions, such that the alkaline solution is supplied to and mixed in a front end, and the carbon dioxide is injected in a rear end. When the alkaline solution is supplied and the pH rises to a level of 12.5, the calcium dissolved in the concentrated water is converted into calcium hydroxide, and is then converted into calcium carbonate upon meeting the carbon dioxide.

[0079] As mentioned above, in the continuous process, since it is difficult to maintain the pH appropriately using a sensor, it is necessary to determine the supply amount of the alkaline solution in advance. Accordingly, in the present embodiment, the amount of the sodium hydroxide solution is determined such that the number of moles of sodium hydroxide is in a range of 1.8 to 2.2 times relative to the number of moles of calcium contained in the concentrated water supplied per unit time, and the sodium hydroxide solution is continuously supplied at a constant rate during the unit time. In addition, Equation (1) described above may also be applied to a calcium carbonate conversion process to determine the injection amount of carbon dioxide (injection amount/second). However, in Equation (1), matters related to magnesium, that is, concentration and molecular weight, may be replaced with those related to calcium, and the target mineral coefficient may be eliminated.

[0080] In addition, the carbon dioxide is injected in the form of microbubbles so as to improve the reaction efficiency with the calcium. That is, the carbon dioxide is pressurized to a pressure of 5 bar or less (4 to 5 bar) and injected after being made into a size having a particle diameter of 50 μm or less (1 to 50 μm), and more preferably is injected at 10 μm or less. This is because, when the carbon dioxide is made into a micro

size, the surface area of the carbon dioxide is widened, and the contact with the calcium becomes more active, thereby improving the calcium carbonate production efficiency.

[0081] When calcium carbonate is formed in the second reactor, the concentrated water is transferred to a second solid-liquid separator to separate the solid-state calcium carbonate therefrom. In the present embodiment, the second solid-liquid separator is configured as a continuous process using a filter press. Of course, the calcium carbonate separation process can also be performed in a batch type rather than in a continuous type.

[0082] Meanwhile, the concentrated water discharged from the second solid-liquid separator may be treated by a chlor-alkali process, similarly to the first embodiment. That is, also in the second embodiment, similarly to the first embodiment, the liquid-phase concentrated water discharged from the second solid-liquid separator is introduced into the chlor-alkali process to produce sodium hydroxide, hydrogen, and chlorine, thereby reducing the concentration of sodium in the concentrated water. In addition, the sodium hydroxide produced herein can be reused as the alkaline solution in the first reactor and the second reactor to achieve a circulating process. Since the chlor-alkali process is the same as that described in the first embodiment, a separate description thereof will be omitted.

[0083] Furthermore, prior to introducing the concentrated water into the chlor-alkali process, the hydrogel described above may be introduced into the concentrated water discharged through the second solid-liquid separator to remove divalent ions remaining in the concentrated water. Of course, although the magnesium and calcium have already been removed through the carbonation process in the second embodiment, since some residual divalent ions remain, the hydrogel may additionally be introduced.

[0084] As described above, in the first embodiment and the second embodiment of the present invention, an alkaline solution is supplied to the concentrated water generated in the seawater desalination plant to form magnesium hydroxide, and the magnesium hydroxide is then reacted with carbon dioxide to produce high-purity magnesium carbonate that is usable as an industrial raw material, and during this process, carbon dioxide, which is a greenhouse gas, is removed.

[0085] In the first embodiment, the calcium in the concentrated water may be reacted with the hydrogel to produce a hydrogel composition for removing carbon dioxide. The hydrogel composition containing the calcium in this manner is subsequently reacted with carbon dioxide to form calcium carbonate, thereby increasing the carbon dioxide treatment amount. In addition, in the second embodiment, the calcium in the concentrated water can be again reacted with carbon dioxide to form calcium carbonate, thereby increasing the carbon dioxide treatment amount.

[0086] With respect to the sodium-rich concentrated water from which the magnesium and calcium have been removed, sodium hydroxide and chlorine gas are produced and recycled through a chlor-alkali process, thereby forming a circulating process. In addition, since the sodium in the concentrated water is consumed as the sodium hydroxide is formed, there is an advantage that the TDS standard can be met when the concentrated water is disposed of.

[0087] The scope of protection of the present invention is not limited to the description and expression of the embodiments explicitly described above. In addition, it is once again added that the scope of protection of the present invention cannot be limited

due to changes or substitutions that are obvious in the technical field to which the present invention belongs.

WHAT IS CLAIMED IS:

1. A method for producing magnesium carbonate using seawater desalination brine, comprising: (A) a step of continuously supplying the seawater desalination brine and an alkaline solution to a first reactor and reacting them, thereby forming solid-state magnesium hydroxide; (B) a step of continuously separating and discharging the solid-state magnesium hydroxide from the concentrated water continuously supplied from the first reactor to a first solid-liquid separator; (C) a step of transferring the concentrated water discharged from the first solid-liquid separator to a second reactor and introducing a polymer hydrogel to bind and remove residual magnesium and calcium in the concentrated water; (D) a step of mixing water with the magnesium hydroxide discharged from the first solid-liquid separator to form a mixed liquid, and supplying the mixed liquid together with carbon dioxide to a third reactor to precipitate magnesium carbonate; (E) a step of supplying the mixed liquid from the third reactor to a third solid-liquid separator to separate and discharge the magnesium carbonate; and (F) a step of producing sodium hydroxide, hydrogen, and chlorine, through a chlor-alkali process, with respect to the concentrated water discharged from the second reactor, to reduce a concentration of sodium in the concentrated water.

2. A method for producing magnesium carbonate using seawater desalination brine, comprising: (A) a step of continuously supplying the seawater desalination brine and an alkaline solution to a first reactor and reacting them, thereby forming solid-state magnesium hydroxide; (B) a step of continuously separating and discharging the solid-state magnesium hydroxide from the concentrated water continuously supplied from the first reactor to a first solid-liquid separator; (C) a step of supplying, together with the concentrated water discharged from the first solid-liquid separator, an alkaline solution and carbon dioxide to a second reactor, thereby forming calcium

carbonate in a solid state; (D) a step of separating the calcium carbonate from the concentrated water supplied from the second reactor to a second solid-liquid separator; (E) a step of mixing water with the magnesium hydroxide discharged from the first solid-liquid separator to form a mixed liquid, and supplying the mixed liquid together with carbon dioxide to a third reactor to precipitate magnesium carbonate; (F) a step of supplying the mixed liquid from the third reactor to a third solid-liquid separator to separate and discharge the magnesium carbonate; and (G) a step of producing sodium hydroxide, hydrogen, and chlorine, through a chlor-alkali process, with respect to the concentrated water discharged in a liquid phase from the second solid-liquid separator, to reduce a concentration of sodium in the concentrated water.

3. The method of claim 1 or 2, wherein the carbon dioxide supplied to the third reactor is in the form of microbubbles having a particle diameter of 50 micrometers or less, and the microbubbles are supplied while being pressurized to 5 bar or less.

4. The method of claim 1 or 2, wherein the alkaline solution supplied to the first reactor is supplied at a ratio of 1.8 to 2.2 times relative to a number of moles (mol) of magnesium in the concentrated water.

5. The method of claim 1 or 2, wherein the first reactor has an inlet formed on one side and an outlet formed on the other side, and includes a tubular stirring section in which a plurality of protrusions are formed protruding on an inner peripheral surface so as to generate a turbulent flow

in the concentrated water.

6. The method of claim 5, wherein the first reactor includes a reaction section disposed at a rear end of the tubular stirring section, in which the magnesium hydroxide is formed.

7. The method of claim 5, further comprising a spray nozzle that is inserted into an inside of the tubular stirring section and supplies the alkaline solution along a flow direction of the concentrated water.

8. The method of claim 1 or 2, wherein the first solid-liquid separator comprises: a chamber having a shape in which a diameter increases from an upper side toward a lower side and then decreases again, the chamber being provided with a space portion therein for mutually separating solid and liquid of the concentrated water, an inlet through which the concentrated water flows in being formed at a lower portion thereof, a discharge hole being formed at an upper central portion thereof, and a slit being formed in a region of largest diameter; a shutter installed in the space portion inside the chamber so as to be vertically movable between a first position closing the slit and a second position opening the slit; and a cover portion in which a flow path for guiding the solid discharged through the slit of the chamber is formed; wherein, while the shutter rotates with the slit closed, the liquid in the concentrated water is continuously discharged through the discharge hole, and the solid in the concentrated water moves to a portion of largest diameter in the chamber and is discharged through the slit when the shutter is spaced downward.

9. The method of claim 1 or 2, wherein the mixed liquid is continuously supplied to and discharged from the third reactor,

$$V_{gas}(L/sec) = \frac{22.4 \cdot V_w(L/sec) \cdot C_{mg}(mol/L) \cdot A}{T_{co2} \cdot P_{co2} \cdot z} \quad \dots \text{Equation (1)}$$

(where V_{gas} is a gas injection amount per unit time, V_w is a mixed liquid injection amount per unit time, C_{mg} is a molar concentration of magnesium in the mixed liquid, A is a volume correction coefficient of carbon dioxide, T_{co2} is a conversion rate at which the carbon dioxide participates in a carbonation reaction (0.01 to 1), P_{co2} is a concentration of carbon dioxide in flue gas (0.01 to 1 as a volume ratio), z is a target mineral coefficient (0.5, 0.8, 1) that determines a specific form of the magnesium carbonate to be produced, and 22.4 is a volume (L) of 1 mole of an ideal gas), and an injection amount per unit time of a gas containing carbon dioxide supplied to the third reactor is determined by Equation (1) above.

10. The method of claim 1 or 2, wherein the water mixed with the magnesium hydroxide is fresh water.

11. The method of claim 10, wherein the mixed liquid discharged from the third solid-liquid separator is supplied again to the third reactor to be circulated.

12. The method of claim 1 or 2, wherein sodium hydroxide and chlorine generated in the chlor-alkali process are mixed to form sodium hypochlorite.

13. The method of claim 1 or 2, wherein, when the concentration of the sodium hydroxide produced in the chlor-alkali process is 10 mass% or more, carbon dioxide is injected into the sodium hydroxide to additionally produce sodium bicarbonate (NaHCO_3) or sodium carbonate (Na_2CO_3).