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(54) Title: CARBON DIOXIDE SEQUESTRATION INVOLVING TWO-SALT-BASED THERMOLYTIC PROCESSES

(57) Abstract: The present invention relates to an energy efficient carbon dioxide sequestration processes whereby calcium silicate minerals and CO₂ are converted into limestone and sand using a two-salt thermolytic process that allows for the cycling of heat and chemicals from one step to another. In one embodiment, MgCl₂ is reacted with water under conditions to form Mg(OH)₂; and the Mg(OH)₂ product is further reacted with CaCl₂ and carbon dioxide to form MgCl₂, CaCO₃, and water.



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DESCRIPTION

CARBON DIOXIDE SEQUESTRATION INVOLVING TWO-SALT-BASED THERMOLYTIC PROCESSES

BACKGROUND OF THE INVENTION

5 This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 61/585,597, filed January 11, 2012, hereby incorporated by reference in its entirety.

I. Field of the Invention

The present invention generally relates to the field of removing carbon dioxide from a source, such as the waste stream (e.g. flue gas) of a power plant, whereby Group 2 silicate
10 minerals are converted into Group 2 chloride salts and SiO₂, Group 2 chloride salts are converted into Group 2 hydroxide and/or Group 2 hydroxychloride salts. These in turn may be reacted with carbon dioxide to form Group 2 carbonate salts, optionally in the presence of catalysts. These steps may be combined to form a cycle in which carbon dioxide is sequestered in the form of carbonate salts and byproducts from one or more steps, such as
15 heat and chemicals, are re-used or recycled in one or more other steps.

II. Description of Related Art

Considerable domestic and international concern has been increasingly focused on the emission of CO₂ into the air. In particular, attention has been focused on the effect of this gas on the retention of solar heat in the atmosphere, producing the "greenhouse effect." Despite
20 some debate regarding the magnitude of the effect, all would agree there is a benefit to removing CO₂ (and other chemicals) from point-emission sources, especially if the cost for doing so were sufficiently small.

Greenhouse gases are predominately made up of carbon dioxide and are produced by municipal power plants and large-scale industry in site-power-plants, though they are also
25 produced in any normal carbon combustion (such as automobiles, rain-forest clearing, simple burning, *etc.*). Though their most concentrated point-emissions occur at power-plants across the planet, making reduction or removal from those fixed sites an attractive point to effect a removal-technology. Because energy production is a primary cause of greenhouse gas emissions, methods such as reducing carbon intensity, improving efficiency, and sequestering

carbon from power-plant flue-gas by various means has been researched and studied intensively over the last thirty years.

Attempts at sequestration of carbon (in the initial form of gaseous CO₂) have produced many varied techniques, which can be generally classified as geologic, terrestrial, or ocean systems. An overview of such techniques is provided in the *Proceedings of First National Conference on Carbon Sequestration*, (2001). To date, many if not all of these techniques are too energy intensive and therefore not economically feasible, in many cases consuming more energy than the energy obtained by generating the carbon dioxide. Alternative processes that overcome one or more of these disadvantages would be advantageous.

The referenced shortcomings are not intended to be exhaustive, but rather are among many that tend to impair the effectiveness of previously known techniques for removing carbon dioxide from waste streams; however, those mentioned here are sufficient to demonstrate that the methodologies appearing in the art have not been altogether satisfactory and that a significant need exists for the techniques described and claimed in this disclosure.

SUMMARY OF THE INVENTION

Disclosed herein are methods and apparatuses for carbon dioxide sequestration, including removing carbon dioxide from waste streams.

In one aspect there are provided methods of sequestering carbon dioxide produced by a source, comprising:

- (a) reacting MgCl₂ or a hydrate thereof with water in a first admixture under conditions suitable to form a first product mixture comprising a first step (a) product comprising Mg(OH)Cl and a second step (a) product comprising HCl;
- (b) reacting some or all of the Mg(OH)Cl from step (a) with a quantity of water and a quantity of MgCl₂ in a second admixture under conditions suitable to form a second product mixture comprising a first step (b) product comprising Mg(OH)₂ and a second step (b) product comprising MgCl₂, wherein the quantity of water is sufficient to provide a molar ratio of water to MgCl₂ of greater than or equal to 6 to 1 in the second product mixture;
- (c) admixing some or all of the Mg(OH)₂ from the first step (b) product with CaCl₂ or a hydrate thereof and carbon dioxide produced by the source in a third admixture under conditions suitable to form a third product mixture comprising a first step (c) product

comprising MgCl_2 or a hydrate thereof, a second step (c) product comprising CaCO_3 , and a third step (c) product comprising water; and
(d) separating some or all of the CaCO_3 from the third product mixture, whereby some or all of the carbon dioxide is sequestered as CaCO_3 .

5 In certain embodiments, the MgCl_2 of step (a) is a MgCl_2 hydrate (*e.g.*, $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$). In some embodiments, the MgCl_2 of step (a) is greater than 90% by weight $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$. In still further embodiments, some or all of the MgCl_2 formed in step (b) and/or step (c) is the MgCl_2 used in step (a). Thus, in certain embodiments, some or all of the water in step (a) is present in the form of a hydrate of the MgCl_2 or is obtained from the water
10 of step (c) or step (b). In certain embodiments, some or all of the water in step (a) is present in the form of steam or supercritical water. In some embodiments some or all of the hydrogen chloride of step (a) is admixed with water to form hydrochloric acid. In a further embodiment the first step (a) product comprises greater than 90% by weight $\text{Mg}(\text{OH})\text{Cl}$. In certain embodiments step (a) occurs in one, two or three reactors.

15 In some embodiments, a defined quantity of water is maintained in the second product mixture of step (b). For example, in some embodiments, the molar ratio of water to MgCl_2 in the second product mixture is between about 6 and about 10, between about 6 and 9, between about 6 and 8, between about 6 and 7 or is about 6. In certain embodiments, a method comprises monitoring the concentration of MgCl_2 in the second product mixture, the quantity
20 of water in the second product mixture or both. In still further embodiments, the amount MgCl_2 and/or water in step (b) (or the flow rates of MgCl_2 and/or water into the second admixture) is adjusted based on such monitoring.

In a further embodiment, a method comprises separating the step (b) products. For example, the $\text{Mg}(\text{OH})_2$ product of step (b) can be a solid and separating the step (b) products
25 can comprise separating some or all of the solid $\text{Mg}(\text{OH})_2$ from the water and MgCl_2 solution. Thus, in some embodiments, the MgCl_2 product of step (b) is aqueous MgCl_2 .

In yet a further embodiment step (b) comprises reacting some or all of the $\text{Mg}(\text{OH})\text{Cl}$ from step (a) with MgCl_2 and a quantity of water in a second admixture under conditions suitable to form a second product mixture comprising a first step (b) product comprising
30 $\text{Mg}(\text{OH})_2$ and a second step (b) product comprising MgCl_2 , wherein the quantity of water is sufficient to provide a molar ratio of water to Mg of greater than or equal to 6 to 1 in said

second admixture. In some embodiments, the some or all of the MgCl_2 for the reaction of step (b) is the MgCl_2 product of step (c).

In a further embodiment, step (c) further comprises admixing sodium hydroxide salt in the third admixture.

5 In still yet a further embodiment, a method comprises:

- (e) admixing a calcium silicate mineral with HCl under conditions suitable to form a third product mixture comprising CaCl_2 , water, and silicon dioxide.

10 For example, in some cases, some or all of the HCl in step (e) is obtained from step (a). In certain embodiments, step (e) further comprises agitating the calcium silicate mineral with HCl. In some embodiments, some or all of the heat generated in step (e) is recovered. In certain embodiments, some or all of the CaCl_2 of step (c) is the CaCl_2 of step (e). In further embodiments, a method comprises a separation step, wherein the silicon dioxide is removed from the CaCl_2 formed in step (e). In yet further embodiments, some or all of the water of step (a) and/or (b) is obtained from the water of step (e).

15 Certain aspects of the embodiments comprise use of a calcium silicate mineral, such as a calcium inosilicate. In some embodiments, the calcium silicate mineral comprises diopside ($\text{CaMg}[\text{Si}_2\text{O}_6]$), tremolite $\text{Ca}_2\text{Mg}_5\{[\text{OH}]\text{Si}_4\text{O}_{11}\}_2$ or CaSiO_3 . In some embodiments, the calcium silicate further comprises iron (*e.g.*, fayalite ($\text{Fe}_2[\text{SiO}_4]$)) and or manganese silicates.

20 In some embodiments, the carbon dioxide is in the form of flue gas, wherein the flue gas further comprises N_2 and H_2O .

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 200 °C to about 500 °C. In some embodiments, the temperature is from about 230 °C to about 260 °C. In some embodiments, the temperature is about 250 °C. In some
25 embodiments, the temperature is from about 200 °C to about 250 °C. In some embodiments, the temperature is about 240 °C.

In some embodiments, suitable reacting conditions of step (b) comprise a temperature from about 140 °C to about 240 °C.

30 In some embodiments, suitable reacting conditions of step (c) comprise a temperature from about 20 °C to about 100 °C. In some embodiments, the temperature is from about 25 °C to about 95 °C.

In some embodiments, suitable reacting conditions of step (e) comprise a temperature from about 50 °C to about 200 °C. In some embodiments, the temperature is from about 90 °C to about 150 °C.

In further aspect there are provided methods of sequestering carbon dioxide produced by a source, comprising:

- (a) reacting a first cation-based halide, sulfate or nitrate salt or hydrate thereof with water in a first admixture under conditions suitable to form a first product mixture comprising a first step (a) product comprising a first cation-based hydroxide salt, a first cation-based oxide salt and/or a first cation-based hydroxychloride salt and a second step (a) product comprising HCl, H₂SO₄ or HNO₃;
- (b) admixing some or all of the first step (a) product with a second cation-based halide, sulfate or nitrate salt or hydrate thereof and carbon dioxide produced by the source in a second admixture under conditions suitable to form a second product mixture comprising a first step (b) product comprising a first cation-based halide, sulfate and/or nitrate salt or hydrate thereof, a second step (b) product comprising a second cation-based carbonate salt, and a third step (b) product comprising water; and
- (c) separating some or all of the second cation-based carbonate salt from the second product mixture,

whereby the carbon dioxide is sequestered into a mineral product form.

In some embodiments, the first cation-based halide sulfate or nitrate salt or hydrate thereof of step (a) is a first cation-based chloride salt or hydrate thereof, and the second step (a) product is HCl. In some embodiments, the first cation-based halide, sulfate, or nitrate salt or hydrate thereof of step (b) is a first cation-based chloride salt or hydrate thereof.

In some embodiments, the first cation-based chloride salt or hydrate thereof of step (a) is MgCl₂. In some embodiments, the first cation-based chloride salt or hydrate thereof of step (a) is a hydrated form of MgCl₂. In some embodiments, the first cation-based chloride salt or hydrate thereof of step (a) is MgCl₂·6H₂O. In some embodiments, the first cation-based hydroxide salt of step (a) is Mg(OH)₂. In some embodiments, the first cation-based hydroxychloride salt of step (a) is Mg(OH)Cl. In some embodiments, the first step (a) product comprises predominantly Mg(OH)Cl. In some embodiments, the first step (a) product comprises greater than 90% by weight Mg(OH)Cl. In some embodiments, the first step (a) product is Mg(OH)Cl. In some embodiments, the first cation-based oxide salt of step (a) is MgO.

In some embodiments, the second cation-based halide, sulfate or nitrate salt or hydrate thereof of step (b) is a second cation-based chloride salt or hydrate thereof, for example, CaCl_2 . In some embodiments, the first cation-based chloride salt of step (b) is MgCl_2 . In some embodiments, the first cation-based chloride salt of step (b) is a hydrated form of MgCl_2 . In some embodiments, the first cation-based chloride salt of step (b) is $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

In some embodiments, some or all of the water in step (a) is present in the form of steam or supercritical water. In some embodiments, some or all of the water of step (a) is obtained from the water of step (b). In some embodiments, step (b) further comprises admixing sodium hydroxide salt in the second admixture.

In some embodiments, the methods further comprise:

- (d) admixing a Group 2 silicate mineral with HCl under conditions suitable to form a third product mixture comprising a Group 2 chloride salt, water, and silicon dioxide.

In some embodiments, some or all of the HCl in step (d) is obtained from step (a). In some embodiments, the methods of step (d) further comprises agitating the Group 2 silicate mineral with HCl. In some embodiments, some or all of the heat generated in step (d) is recovered. In some embodiments, some or all of the second cation-based chloride salt of step (b) is the Group 2 chloride salt of step (d). In some embodiments, the methods further comprise a separation step, wherein the silicon dioxide is removed from the Group 2 chloride salt formed in step (d). In some embodiments, some or all of the water of step (a) is obtained from the water of step (d).

In some embodiments, the Group 2 silicate mineral of step (d) comprises a Group 2 inosilicate. In some embodiments, the Group 2 silicate mineral of step (d) comprises CaSiO_3 . In some embodiments, the Group 2 silicate mineral of step (d) comprises MgSiO_3 . In some embodiments, the Group 2 silicate mineral of step (d) comprises olivine ($\text{Mg}_2[\text{SiO}_4]$). In some embodiments, the Group 2 silicate mineral of step (d) comprises serpentine ($\text{Mg}_6[\text{OH}]_8[\text{Si}_4\text{O}_{10}]$). In some embodiments, the Group 2 silicate mineral of step (d) comprises sepiolite ($\text{Mg}_4[(\text{OH})_2\text{Si}_6\text{O}_{15}] \cdot 6\text{H}_2\text{O}$), enstatite ($\text{Mg}_2[\text{Si}_2\text{O}_6]$), diopside ($\text{CaMg}[\text{Si}_2\text{O}_6]$), and/or tremolite $\text{Ca}_2\text{Mg}_5\{[\text{OH}]\text{Si}_4\text{O}_{11}\}_2$. In some embodiments, the Group 2 silicate further comprises iron and or manganese silicates. In some embodiments, the iron silicate is fayalite ($\text{Fe}_2[\text{SiO}_4]$).

In some embodiments, some or all of the first cation-based chloride salt formed in step (b) is the first cation-based chloride salt used in step (a).

In some embodiments, the carbon dioxide is in the form of flue gas, wherein the flue gas further comprises N_2 and H_2O .

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 200 °C to about 500 °C. In some embodiments, the temperature is from about 230 °C to about 260 °C. In some embodiments, the temperature is about 250 °C. In some embodiments, the temperature is from about 200 °C to about 250 °C. In some embodiments, the temperature is about 240 °C.

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 50 °C to about 200 °C. In some embodiments, the temperature is from about 90 °C to about 260 °C. In some embodiments, the temperature is from about 90 °C to about 230 °C. In some embodiments, the temperature is about 130 °C.

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 400 °C to about 550 °C. In some embodiments, the temperature is from about 450 °C to about 500 °C.

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 20 °C to about 100 °C. In some embodiments, the temperature is from about 25 °C to about 95 °C.

In some embodiments, suitable reacting conditions of step (a) comprise a temperature from about 50 °C to about 200 °C. In some embodiments, the temperature is from about 90 °C to about 150 °C.

In another aspect, the present invention provides methods of sequestering carbon dioxide produced by a source, comprising:

- (a) admixing a magnesium chloride salt and water in a first admixture under conditions suitable to form (i) magnesium hydroxide, magnesium oxide and/or $Mg(OH)Cl$ and (ii) hydrogen chloride;
- (b) admixing (i) magnesium hydroxide, magnesium oxide and/or $Mg(OH)Cl$, (ii) $CaCl_2$ and (iii) carbon dioxide produced by the source in a second admixture under conditions suitable to form (iv) calcium carbonate, (v) a magnesium chloride salt, and (vi) water; and
- (c) separating the calcium carbonate from the second admixture, whereby the carbon dioxide is sequestered into a mineral product form.

In some embodiments, some or all of the hydrogen chloride of step (a) is admixed with water to form hydrochloric acid. In some embodiments, some or all of the magnesium hydroxide, magnesium oxide and/or $Mg(OH)Cl$ of step (b)(i) is obtained from step (a)(i). In

some embodiments, some of all the water in step (a) is present in the form of a hydrate of the magnesium chloride salt. In some embodiments, step (a) occurs in one, two or three reactors. In some embodiments, step (a) occurs in one reactor. In some embodiments, the magnesium hydroxide, magnesium oxide and/or $\text{Mg}(\text{OH})\text{Cl}$ of step (a)(i) is greater than 90% by weight $\text{Mg}(\text{OH})\text{Cl}$. In some embodiments, the magnesium chloride salt is greater than 90% by weight $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$.

In some embodiments, the methods further comprise:

- (d) admixing a Group 2 silicate mineral with hydrogen chloride under conditions suitable to form a Group 2 chloride salt, water, and silicon dioxide.

In some embodiments, some or all of the hydrogen chloride in step (d) is obtained from step (a). In some embodiments, step (d) further comprises agitating the Group 2 silicate mineral with the hydrochloric acid. In some embodiments, some or all of the magnesium chloride salt in step (a) is obtained from step (d). In some embodiments, the methods further comprise a separation step, wherein the silicon dioxide is removed from the Group 2 chloride salt formed in step (d). In some embodiments, some or all of the water of step (a) is obtained from the water of step (d). In some embodiments, the Group 2 silicate mineral of step (d) comprises a Group 2 inosilicate.

In some embodiments, the Group 2 silicate mineral of step (d) comprises CaSiO_3 . In some embodiments, the Group 2 silicate mineral of step (d) comprises MgSiO_3 . In some embodiments, the Group 2 silicate mineral of step (d) comprises olivine. In some embodiments, the Group 2 silicate mineral of step (d) comprises serpentine. In some embodiments, the Group 2 silicate mineral of step (d) comprises sepiolite, enstatite, diopside, and/or tremolite. In some embodiments, the Group 2 silicate further comprises mineralized iron and or manganese.

In some embodiments, step (b) further comprises admixing CaCl_2 and water to the second admixture.

Other objects, features and advantages of the present disclosure will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating specific embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present disclosure. The invention may be better understood by reference to one of these drawings in combination with the detailed description of specific embodiments presented herein.

FIG. 1 is block diagram of a system for a Group 2 hydroxide-based process to sequester CO₂ as Group 2 carbonates according to some embodiments of the present invention.

FIG. 2 is block diagram of a system in which Mg²⁺ functions as a catalyst for the sequestration of CO₂ as calcium carbonate according to some embodiments of the present invention.

FIG. 3 is a simplified process flow diagram according to some embodiments of the processes provided herein. Shown is a Group-II hydroxide-based process, which sequesters CO₂ as limestone (composed largely of the mineral calcite, CaCO₃). The term “road salt” in this figure refers to a Group II chloride, such as CaCl₂ and/or MgCl₂, either or both of which are optionally hydrated. In embodiments comprising MgCl₂, heat may be used to drive the reaction between road salt and water (including water of hydration) to form HCl and magnesium hydroxide, Mg(OH)₂, and/or magnesium hydroxychloride, Mg(OH)Cl. In embodiments comprising CaCl₂, heat may be used to drive the reaction between road salt and water to form calcium hydroxide and HCl. The HCl is reacted with, for example, calcium inosilicate rocks (optionally ground), to form additional road salt, *e.g.*, CaCl₂, and sand (SiO₂).

FIG. 4 is a simplified process-flow diagram corresponding to some embodiments of the present invention. Silicate rocks may be used in some embodiments of the present invention to sequester CO₂ as CaCO₃. The term “road salt” in this figure refers to a Group II chloride, such as CaCl₂ and/or MgCl₂, either or both of which are optionally hydrated. In the road salt boiler, heat may be used to drive the reaction between road salt, *e.g.*, MgCl₂·6H₂O, and water (including water of hydration) to form HCl and Group II hydroxides, oxides, and/or mixed hydroxide-chlorides, including, for example, magnesium hydroxide, Mg(OH)₂, and/or magnesium hydroxychloride, Mg(OH)Cl. In embodiments comprising CaCl₂, heat may be used to drive the reaction between road salt and water to form calcium hydroxide and HCl. The HCl may be sold or reacted with silicate rocks, *e.g.*, inosilicates, to form additional

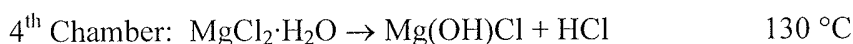
road salt, *e.g.*, CaCl_2 , and sand (SiO_2). Ion exchange reaction between Mg^{2+} and Ca^{2+} may be used, in some of these embodiments, to allow, for example, the cycling of Mg^{2+} ions.

FIG. 5 is a process flow diagram showing parameters and results from a process simulation using Aspen Plus process software. In this embodiment, a 35% MgCl_2 , 65% H_2O solution is heated to 536 °F (280 °C), then the stream leaves in the stream labeled “ H_2O - MgOH ,” which comprises a solution of MgCl_2 and solid $\text{Mg}(\text{OH})_2$. Typically, when $\text{Mg}(\text{OH})\text{Cl}$ dissolves in water it forms $\text{Mg}(\text{OH})_2$ (solid) and MgCl_2 (dissolved). Here the MgCl_2 is not used to absorb CO_2 directly, rather it is recycled. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, CaCl_2 and water, to form CaCO_3 . Results from the simulation suggest that it is efficient to recirculate a MgCl_2 stream and then to react it with H_2O and heat to form $\text{Mg}(\text{OH})_2$. One or more of the aforementioned compounds then reacts with a $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to ultimately form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to repeat the process.

FIG. 6 is a process flow diagram showing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, CaCl_2 and water, to form CaCO_3 . In this embodiment, the hexahydrate is dehydrated in three separate chambers and decomposed in the fourth chamber where the HCl that is formed from the decomposition is recirculated back to the third chamber to prevent any side reactions. Reactions occurring in these chambers include the following:



(HCl vapor present)



HCl recirculates to the 3rd chamber.

Chamber	Reaction	Model Temp.	Preferred Temp. Range	Notes
1 st	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$	100°C	90°C-120°C	
2 nd	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$	125°C	160°C-185°C	
3 rd	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$	160°C	190°C- 230°C	*

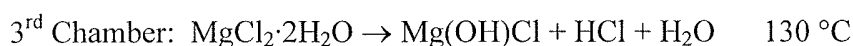
4 th	$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}$	130°C	230°C- 260°C	**
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* HCl Vapor Present

** HCl Vapor Recirculates to the 3rd Chamber

The first three reactions above may be characterized as dehydrations, while the fourth may be characterized as a decomposition. Results from this simulation, which is explained in greater detail in Example 2, indicate that at lower temperatures (130-250 °C) the decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ results in the formation of $\text{Mg}(\text{OH})\text{Cl}$ instead of MgO . The $\text{Mg}(\text{OH})\text{Cl}$ then reacts with H_2O to form MgCl_2 and $\text{Mg}(\text{OH})_2$, which then reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again.

FIG. 7 is a process flow diagram showing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, CaCl_2 and water, to form CaCO_3 . In this embodiment, the magnesium hexahydrate is dehydrated in two separate chambers and decomposed in a third chamber. Both dehydration and decomposition reactions occur in the third chamber. There is no recirculating HCl. Reactions occurring in these chambers include the following:



Chamber	Reaction	Model Temp.	Preferred Temp. Range	Notes
1 st	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$	100°C	90°C-120°C	
2 nd	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$	125°C	160°C-185°C	
3 rd	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + \text{H}_2\text{O}$	130°C	190°C- 230°C	*
	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$			

* No recirculating HCl

The first, second and fourth reactions above may be characterized as dehydrations, while the third may be characterized as a decomposition. As in the embodiment of FIG. 6, the temperatures used in this embodiment result in the formation of $\text{Mg}(\text{OH})\text{Cl}$ from the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ rather than MgO . The $\text{Mg}(\text{OH})\text{Cl}$ then reacts with H_2O to form MgCl_2 and $\text{Mg}(\text{OH})_2$, which reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to

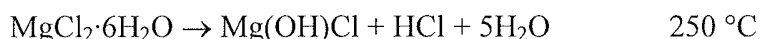
form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again. Additional details regarding this simulation are provided in Example 3 below.

FIG. 8 is a process flow diagram showing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, CaCl_2 and water, to form CaCO_3 . Results from this simulation indicate that it is efficient to heat $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to form MgO . The MgO then reacts with H_2O to form $\text{Mg}(\text{OH})_2$, which then reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again. In this embodiment, the magnesium hexahydrate is simultaneously dehydrated and decomposed in one chamber at 450°C . This is the model temperature range. The preferred range in some embodiments, is $450^\circ\text{C} - 500^\circ\text{C}$. Thus the decomposition goes completely to MgO . The main reaction occurring in this chamber can be represented as follows:



Additional details regarding this simulation are provided in Example 4 below.

FIG. 9 is a process flow diagram showing parameters and results from a process simulation using Aspen Plus process software similar to the embodiment of FIG. 8 except that the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is decomposed into an intermediate compound, $\text{Mg}(\text{OH})\text{Cl}$ at a lower temperature of 250°C in one chamber. The $\text{Mg}(\text{OH})\text{Cl}$ is then dissolved in water to form MgCl_2 and $\text{Mg}(\text{OH})_2$, which follows through with the same reaction with CaCl_2 and CO_2 to form CaCO_3 and MgCl_2 . The main reaction occurring in this chamber can be represented as follows:



The reaction was modeled at 250°C . In some embodiments, the preferred range is from 230°C to 260°C . Additional details regarding this simulation are provided in Example 5 below.

FIG. 10 shows a graph of the mass percentage of a heated sample of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The sample's initial mass was approximately 70 mg and set at 100%. During the experiment, the sample's mass was measured while it was being thermally decomposed. The temperature was quickly ramped up to 150°C , and then slowly increased by 0.5°C per minute. At approximately 220°C , the weight became constant, consistent with the formation of $\text{Mg}(\text{OH})\text{Cl}$.

FIG. 11 shows X-ray diffraction data corresponding to the product of Example 7.

FIG. 12 shows X-ray diffraction data corresponding to the product from the reaction using $\text{Mg}(\text{OH})_2$ of Example 8.

FIG. 13 shows X-ray diffraction data corresponding to the product from the reaction
5 using $\text{Mg}(\text{OH})\text{Cl}$ of Example 8.

FIG. 14 shows the effect of temperature and pressure on the decomposition of $\text{MgCl}_2 \cdot (\text{H}_2\text{O})$.

FIG. 15 is a process flow diagram of an embodiment of the Ca/Mg process described herein.

10 **FIG. 16** is a process flow diagram of a variant of the process, whereby only magnesium compounds are used. In this embodiment the $\text{Ca}^{2+} - \text{Mg}^{2+}$ switching reaction does not occur.

FIG. 17 is a process flow diagram of a different variant of the process which is in between the previous two embodiments. Half of the Mg^{2+} is replaced by Ca^{2+} , thereby
15 making the resulting mineralized carbonate $\text{MgCa}(\text{CO}_3)_2$ or dolomite.

FIG. 18 – CaSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ Process, Cases 10 & 11. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, CaSiO_3 , CO_2 and water, to form SiO_2 and CaCO_3 . Results from this simulation
20 indicate that it is efficient to use heat from the HCl reacting with CaSiO_3 and heat from the flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to form $\text{Mg}(\text{OH})\text{Cl}$. The $\text{Mg}(\text{OH})\text{Cl}$ then reacts with H_2O to form MgCl_2 and $\text{Mg}(\text{OH})_2$, which then reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled
25 to the first reactor to begin the process again. In this embodiment, the magnesium chloride hexahydrate is dehydrated to magnesium chloride dihydrate $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in the first chamber using heat from the HCl and CaSiO_3 reaction and decomposed in a second chamber at 250°C using heat from the flue gas. Thus the decomposition goes partially to $\text{Mg}(\text{OH})\text{Cl}$. The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH^{**} kJ/mole	Reaction Temp. Range
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + 5\text{H}_2\text{O} + \text{HCl}$	433	230 °C – 260 °C
$2\text{HCl}(\text{g}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	–259	90 °C – 150 °C
$2\text{Mg}(\text{OH})\text{Cl} + \text{CO}_2 + \text{CaCl}_2 \rightarrow 2\text{MgCl}_2 + \text{CaCO}_3\downarrow + \text{H}_2\text{O}$	–266	25 °C – 95 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 10 and 11 below.

FIG. 19 – CaSiO₃-MgO Process, Cases 12 & 13. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO₂ from flue gas using inexpensive raw materials, CaSiO₃, CO₂ and water, to form SiO₂ and CaCO₃. Results from this simulation indicate that it is efficient to use heat from the HCl reacting with CaSiO₃ and heat from flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of MgCl₂·6H₂O to form MgO. The MgO then reacts with H₂O to form Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂ formed is recycled to the first reactor to begin the process again. In this embodiment, the magnesium chloride hexahydrate is dehydrated to magnesium chloride dihydrate MgCl₂·2H₂O in the first chamber using heat from the HCl and CaSiO₃ reaction and decomposed in a second chamber at 450°C using heat from the flue gas. Thus the decomposition goes completely to MgO. The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH kJ/mole**	Reaction Temp. Range
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgO} + 5\text{H}_2\text{O} + 2\text{HCl}$	560	450 °C – 500 °C
$2\text{HCl}(\text{g}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	–264	90 °C – 150 °C
$\text{MgO} + \text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{CaCO}_3\downarrow$	–133	25 °C – 95 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 12 and 13 below.

FIG. 20 – MgSiO₃-Mg(OH)Cl Process, Cases 14 & 15. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO₂ from flue gas using inexpensive raw

materials, MgSiO_3 , CO_2 and water, to form SiO_2 and MgCO_3 . Results from this simulation indicate that it is efficient to use heat from the HCl reacting with MgSiO_3 and heat from the flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ to form Mg(OH)Cl . The Mg(OH)Cl then reacts with H_2O to form MgCl_2 and Mg(OH)_2 , which then reacts with CO_2 from the flue gas to form MgCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again. In this embodiment, the magnesium chloride remains in the dihydrate form $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ due to the heat from the HCl and MgSiO_3 prior to decomposition at 250°C using heat from the flue gas. Thus the decomposition goes partially to Mg(OH)Cl . The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH kJ/mole **	Reaction Temp. Ranges
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)Cl} + \text{H}_2\text{O(g)} + \text{HCl(g)}$	139.8	$230^\circ\text{C} - 260^\circ\text{C}$
$2\text{HCl(g)} + \text{MgSiO}_3 \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	-282.8	$90^\circ\text{C} - 150^\circ\text{C}$
$2\text{Mg(OH)Cl} + \text{CO}_2 \rightarrow \text{MgCl}_2 + \text{MgCO}_3\downarrow + \text{H}_2\text{O}$	-193.1	$25^\circ\text{C} - 95^\circ\text{C}$

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 14 and 15 below.

FIG. 21 – MgSiO_3 - MgO Process, Cases 16 & 17. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, MgSiO_3 , CO_2 and water, to form SiO_2 and MgCO_3 . Results from this simulation indicate that it is efficient to use heat from the HCl reacting with MgSiO_3 and heat from the flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ to form MgO . The MgO then reacts with H_2O to form Mg(OH)_2 , which then reacts with CO_2 from the flue gas to form MgCO_3 , which is filtered out of the stream. In this embodiment, the magnesium chloride remains in the dihydrate form $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ due to the heat from the HCl and MgSiO_3 prior to decomposition at 450°C using heat from the flue gas. Thus the decomposition goes completely to MgO . The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH kJ/mole **	Reaction Temp. Range
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2\text{O}(\text{g}) + 2\text{HCl}(\text{g})$	232.9	450 °C – 500 °C
$2\text{HCl}(\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{g}) + \text{SiO}_2\downarrow$	–293.5	90 °C – 150 °C
$\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3\downarrow$	–100	25 °C – 95 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 16 and 17 below.

FIG. 22 – Diopside-Mg(OH)Cl Process, Cases 18 & 19. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO_2 from flue gas using inexpensive raw materials, diopside $\text{MgCa}(\text{SiO}_3)_2$, CO_2 and water, to form SiO_2 and dolomite $\text{MgCa}(\text{CO}_3)_2$. Results from this simulation indicate that it is efficient to use heat from the HCl reacting with $\text{MgCa}(\text{SiO}_3)_2$ and heat from the flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to form Mg(OH)Cl . The Mg(OH)Cl then reacts with H_2O to form MgCl_2 and Mg(OH)_2 , which then reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to form $\text{MgCa}(\text{CO}_3)_2$ which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again. In this embodiment, the magnesium chloride hexahydrate is dehydrated to magnesium chloride dihydrate $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ in the first chamber using heat from the HCl and CaSiO_3 reaction and decomposed to Mg(OH)Cl in a second chamber at 250°C using heat from the flue gas. The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH kJ/mole**	Reaction Temp. Range
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg(OH)Cl} + 5\text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g})$	433	230 °C – 260 °C
$2\text{HCl}(\text{g}) + \text{MgCa}(\text{SiO}_3)_2 \rightarrow \text{CaCl}_2(\text{aq}) + \text{MgSiO}_3\downarrow + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	–235	90 °C – 150 °C
$2\text{HCl}(\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	–282.8	90 °C – 150 °C
$4\text{Mg(OH)Cl} + 2\text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCa}(\text{CO}_3)_2\downarrow + 3\text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}$	–442	25 °C – 95 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 18 and 19 below.

FIG. 23 – Diopside-MgO Process, Cases 20 & 21. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO₂ from flue gas using inexpensive raw materials, diopside MgCa(SiO₃)₂, CO₂ and water, to form SiO₂ and dolomite MgCa(CO₃)₂. Results from this simulation indicate that it is efficient to use heat from the HCl reacting with MgCa(SiO₃)₂ and heat from the flue gas emitted by a natural gas or coal fired power plant and/or other heat source to carry out the decomposition of MgCl₂·6H₂O to form MgO. The MgO then reacts with H₂O to form Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form MgCa(CO₃)₂ which is filtered out of the stream. The resulting MgCl₂ formed is recycled to the first reactor to begin the process again. In this embodiment, the magnesium chloride hexahydrate is dehydrated to magnesium chloride dihydrate MgCl₂·2H₂O in the first chamber using heat from the HCl and CaSiO₃ reaction and decomposed to MgO in a second chamber at 450°C using heat from the flue gas. The main reactions occurring in this chamber can be represented as follows:

Reaction	ΔH kJ/mole**	Reaction Temp. Range
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgO} + 5\text{H}_2\text{O} + 2\text{HCl}$	560	450 °C – 500 °C
$2\text{HCl}(\text{g}) + \text{MgCa}(\text{SiO}_3)_2 \rightarrow \text{CaCl}_2(\text{g}) + \text{MgSiO}_3\downarrow + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-240	90 °C – 150 °C
$2\text{HCl}(\text{aq}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-288	90 °C – 150 °C
$2\text{MgO} + 2\text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCa}(\text{CO}_3)_2\downarrow + \text{MgCl}_2(\text{aq})$	-258	25 °C – 95 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Additional details regarding this simulation are provided in Examples 20 and 21 below.

FIG. 24 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition. See Examples 10 through 13 of the CaSiO₃-Mg(OH)Cl and CaSiO₃-MgO processes.

FIG. 25 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition. See Examples 14 through 17 of the MgSiO₃-Mg(OH)Cl and MgSiO₃-MgO processes.

FIG. 26 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition. See Examples 18 through 21 of the Diopside - Mg(OH)Cl and Diopside - MgO processes.

FIG. 27 is a simplified process-flow diagram corresponding to some embodiments of the present invention in which two different salts, *e.g.*, Ca²⁺ and Mg²⁺, are used for decomposition and carbonation.

FIGS. 28-29 show graphs of the mass percentages of heated samples of MgCl₂·6H₂O. The initial masses of the samples were approximately 70 mg each and were each set at 100%. During the experiment, the masses of the samples were measured while they were being thermally decomposed. The temperature was ramped up to 200 °C then further increased over the course of a 12 hour run. The identities of the decomposed materials can be confirmed by comparing against the theoretical plateaus provided. FIG. 28 is a superposition of two plots, the first one being the solid line, which is a plot of time (minutes) versus temperature (°C). The line illustrates the ramping of temperature over time; the second plot, being the dashed line is a plot of weight % (100% = original weight of sample) versus time, which illustrates the reduction of the sample's weight over time whether by dehydration or decomposition. FIG. 29 is also a superposition of two plots, the first (the solid line) is a plot of weight% versus temperature (°C), illustrating the sample's weight decreasing as the temperature increases; the second plot (the dashed line) is a plot of the derivative of the weight% with respect to temperature (wt.%/°C) versus temperature °C. When this value is high it indicates a higher rate of weight loss for each change per degree. If this value is zero, the sample's weight remains the same although the temperature is increasing, indicating an absence of dehydration or decomposition. Note Figure 28 and 29 are of the same sample.

FIG. 30 – MgCl₂·6H₂O Decomposition at 500°C after One Hour. This graph shows the normalized final and initial weights of four test runs of MgCl₂·6H₂O after heating at 500 °C for one hour. The consistent final weight confirms that MgO is made by decomposition at this temperature.

FIG. 31 – Three-Chamber Decomposition. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus

process software. In this embodiment, heat from cold flue gas (chamber 1), heat from mineral dissolution reactor (chamber 2), and external natural gas (chamber 3) are used as heat sources. This process flow diagram illustrates a three chamber process for the decomposition to $\text{Mg}(\text{OH})\text{Cl}$. The first chamber is heated by 200 °C flue gas to provide some initial heat about ~8.2% of the total required heat, the second chamber which relies on heat recovered from the mineral dissolution reactor to provide 83% of the needed heat for the decomposition of which 28% is from the hydrochloric acid/mineral silicate reaction and 55% is from the condensation and formation of hydrochloric acid, and finally the third chamber, which uses natural gas as an external source of the remaining heat which is 8.5% of the total heat. The CO_2 is from a combined cycle power natural gas plant, so very little heat is available from the power plant to power the decomposition reaction.

FIG. 32 – Four-Chamber Decomposition. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. In this embodiment, heat from cold flue gas (chamber 1), heat from additional steam (chamber 2), heat from mineral dissolution reactor (chamber 3), and external natural gas (chamber 4) are used as heat sources. This process flow diagram illustrates a four chamber process for the decomposition to $\text{Mg}(\text{OH})\text{Cl}$, the first chamber provides 200 °C flue gas to provide some initial heat about ~8.2% of the total required heat, the second chamber provides heat in the form of extra steam which is 0.8% of the total heat needed, the third chamber which relies on heat recovered from the mineral dissolution reactor to provide 83% of the needed heat for the decomposition of which 28% is from the hydrochloric acid/mineral silicate reaction and 55% is from the condensation and formation of hydrochloric acid, and finally the fourth chamber, which uses natural gas as an external source of the remaining heat which is 8.0% of the total heat. The CO_2 is from a combined cycle natural gas power plant, so very little heat is available from the power plant to power the decomposition reaction.

FIG. 33 – Two-Chamber Decomposition. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. In this embodiment, heat from mineral dissolution reactor (chamber 1), and external natural gas (chamber 2) are used as heat sources. This process flow diagram illustrates a two chamber process for the decomposition to $\text{Mg}(\text{OH})\text{Cl}$, the first chamber which relies on heat recovered from the mineral dissolution reactor to provide 87% of the needed heat for the decomposition of which 28% is from the hydrochloric acid/mineral silicate reaction and 59% is from the condensation and formation of hydrochloric acid, and the second chamber, which uses natural gas as an external source of the remaining heat which

is 13% of the total heat. The CO₂ is from a combined cycle natural gas power plant, so very little heat is available from the power plant to power the decomposition reaction.

FIG. 34 – Two-Chamber Decomposition. This figure shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. In this embodiment, heat from mineral dissolution reactor (chamber 1), and hot flue gas from open cycle natural gas plant (chamber 2) are used as heat sources. This process flow diagram illustrates a two chamber process for the decomposition to Mg(OH)Cl, the first chamber which relies on heat recovered from the mineral dissolution reactor to provide 87% of the needed heat for the decomposition of which 28% is from the hydrochloric acid/mineral silicate reaction and 59% is from the condensation and formation of hydrochloric acid, and the second chamber, which uses hot flue gas as an external source of the remaining heat which is 13% of the total heat. The CO₂ is from an open cycle natural gas power plant, therefore substantial heat is available from the power plant in the form of 600 °C flue gas to power the decomposition reaction.

FIG. 35 shows a schematic diagram of a Auger reactor which may be used for the salt decomposition reaction, including the decomposition of MgCl₂·6H₂O to Mg(OH)Cl or MgO. Such reactors may comprises internal heating for efficient heat utilization, external insulation for efficient heat utilization, a screw mechanism for adequate solid transport (when solid is present), adequate venting for HCl removal. Such a reactors has been used to prepare ~1.8kg of ~90% Mg(OH)Cl.

FIG. 36 shows the optimization index for two separate runs of making Mg(OH)Cl using an Auger reactor. The optimization index = % conversion × % efficiency.

FIG. 37 shows a process flow diagram of an Aspen model that simulates an CaSiO₃-Mg(OH)Cl Process.

FIG. 38A-I shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO₂ from flue gas using inexpensive raw materials, CaSiO₃, CO₂ and water, to form SiO₂ and CaCO₃. Heat is used to carry out the decomposition of MgCl₂·6H₂O to form Mg(OH)Cl. The Mg(OH)Cl then reacts with H₂O to form MgCl₂ and Mg(OH)₂. The quantity of H₂O is regulated to favor formation of solid Mg(OH)₂ and aqueous MgCl₂ (which is recycled to the first reactor to begin the process again). The Mg(OH)₂ then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂ formed is recycled to the first reactor to begin the process again.

A, is an overview diagram of the process. B-I, are overlapping enlargements of the overview diagram shown in A.

FIG. 39A-I shows a process flow diagram providing parameters and results from a process simulation using Aspen Plus process software. The net reaction is the capture of CO₂ from flue gas using inexpensive raw materials, CaSiO₃, CO₂ and water, to form SiO₂ and CaCO₃. Heat is used to carry out the decomposition of MgCl₂·6H₂O to form Mg(OH)Cl. The Mg(OH)Cl then reacts with H₂O to form MgCl₂ and Mg(OH)₂. The quantity of H₂O is regulated to favor formation of solid Mg(OH)₂ and aqueous MgCl₂ (which is recycled to the first reactor to begin the process again). The Mg(OH)₂ then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂ formed is recycled to the first reactor to begin the process again. A, is an overview diagram of the process. B-I, are overlapping enlargements of the overview diagram shown in A.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

The present invention relates to carbon dioxide sequestration, including energy-efficient processes in which Group 2 chlorides are converted to Group 2 hydroxides and hydrogen chloride, which are then used to remove carbon dioxide from waste streams. In some embodiments, hydrogen chloride may be further reacted with Group 2 silicates to produce additional Group 2 chloride starting materials and silica.

In some embodiments, the methods and apparatuses of the invention comprise one or more of the following general components: (1) the conversion of Group 2 silicate minerals with hydrogen chloride into Group 2 chlorides and silicon dioxide, (2) conversion of Group 2 chlorides into Group 2 hydroxides and hydrogen chloride, (3) an aqueous decarbonation whereby gaseous CO₂ is absorbed into an aqueous caustic mixture comprising Group 2 hydroxides to form Group 2 carbonate and/or bicarbonate products and water, (4) a separation process whereby the carbonate and/or bicarbonate products are separated from the liquid mixture, (5) the reuse or cycling of by-products, including energy, from one or more of the steps or process streams into another one or more steps or process streams. Each of these general components is explained in further detail below.

While many embodiments of the present invention consume some energy to accomplish the absorption of CO₂ and other chemicals from flue-gas streams and to accomplish the other objectives of embodiments of the present invention as described herein,

one advantage of certain embodiments of the present invention is that they provide ecological efficiencies that are superior to those of the prior art, while absorbing most or all of the emitted CO₂ from a given source, such as a power plant.

Another additional benefit of certain embodiments of the present invention that distinguishes them from other CO₂-removal processes is that in some market conditions, the products are worth considerably more than the reactants required or the net-power or plant-depreciation costs. In other words, certain embodiments are industrial methods of producing chloro-hydro-carbonate products at a profit, while accomplishing considerable removal of CO₂ and incidental pollutants of concern.

10 I. Definitions

As used herein, the terms “carbonates” or “carbonate products” are generally defined as mineral components containing the carbonate group, [CO₃]²⁻. Thus, the terms encompass both carbonate/bicarbonate mixtures and species containing solely the carbonate ion. The terms “bicarbonates” and “bicarbonate products” are generally defined as mineral components containing the bicarbonate group, [HCO₃]¹⁻. Thus, the terms encompass both carbonate/bicarbonate mixtures and species containing solely the bicarbonate ion.

As used herein “Ca/Mg” signifies either Ca alone, Mg alone or a mixture of both Ca and Mg. The ratio of Ca to Mg may range from 0:100 to 100:0, including, e.g., 1:99, 5:95, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10, 95:5, and 99:1. The symbols “Ca/Mg”, “MgxCa(1-x)” and CaxMg(1-x)” are synonymous. In contrast, “CaMg” or “MgCa” refers to a 1:1 ratio of these two ions.

As used herein, the term “ecological efficiency” is used synonymously with the term “thermodynamic efficiency” and is defined as the amount of CO₂ sequestered by certain embodiments of the present invention per energy consumed (represented by the equation “∂CO₂/∂E”), appropriate units for this value are kWh/ton CO₂. CO₂ sequestration is denominated in terms of percent of total plant CO₂; energy consumption is similarly denominated in terms of total plant power consumption.

The terms “Group II” and “Group 2” are used interchangeably.

“Hexahydrate” refers to MgCl₂·6H₂O.

In the formation of bicarbonates and carbonates using some embodiments of the present invention, the term “ion ratio” refers to the ratio of cations in the product divided by the number of carbons present in that product. Hence, a product stream formed of calcium bicarbonate (Ca(HCO₃)₂) may be said to have an “ion ratio” of 0.5 (Ca/C), whereas a product

stream formed of pure calcium carbonate (CaCO_3) may be said to have an “ion ratio” of 1.0 (Ca/C). By extension, an infinite number of continuous mixtures of carbonate and bicarbonate of mono-, di- and trivalent cations may be said to have ion ratios varying between 0.5 and 3.0.

5 Based on the context, the abbreviation “MW” either means molecular weight or megawatts.

 The abbreviation “PFD” is process flow diagram.

 The abbreviation “Q” is heat (or heat duty), and heat is a type of energy. This does not include any other types of energy.

10 As used herein, the term “sequestration” is used to refer generally to techniques or practices whose partial or whole effect is to remove CO_2 from point emissions sources and to store that CO_2 in some form so as to prevent its return to the atmosphere. Use of this term does not exclude any form of the described embodiments from being considered “sequestration” techniques.

15 In the context of a chemical formula, the abbreviation “W” refers to H_2O .

 The pyroxenes are a group of silicate minerals found in many igneous and metamorphic rocks. They share a common structure consisting of single chains of silica tetrahedra and they crystallize in the monoclinic and orthorhombic systems. Pyroxenes have the general formula $\text{XY}(\text{Si},\text{Al})_2\text{O}_6$, where X represents calcium, sodium, iron (II) and
20 magnesium and more rarely zinc, manganese and lithium and Y represents ions of smaller size, such as chromium, aluminium, iron(III), magnesium, manganese, scandium, titanium, vanadium and even iron (II).

 In addition, atoms making up the compounds of the present invention are intended to include all isotopic forms of such atoms. Isotopes, as used herein, include those atoms
25 having the same atomic number but different mass numbers. By way of general example and without limitation, isotopes of hydrogen include tritium and deuterium, and isotopes of carbon include ^{13}C and ^{14}C .

 The use of the word “a” or “an,” when used in conjunction with the term “comprising” in the claims and/or the specification may mean “one,” but it is also consistent
30 with the meaning of “one or more,” “at least one,” and “one or more than one.”

 Throughout this application, the term “about” is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

The terms “comprise,” “have” and “include” are open-ended linking verbs. Any forms or tenses of one or more of these verbs, such as “comprises,” “comprising,” “has,” “having,” “includes” and “including,” are also open-ended. For example, any method that “comprises,” “has” or “includes” one or more steps is not limited to possessing only those one or more steps and also covers other unlisted steps.

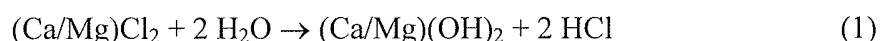
The term “effective,” as that term is used in the specification and/or claims, means adequate to accomplish a desired, expected, or intended result.

The above definitions supersede any conflicting definition in any of the reference that is incorporated by reference herein. The fact that certain terms are defined, however, should not be considered as indicative that any term that is undefined is indefinite. Rather, all terms used are believed to describe the invention in terms such that one of ordinary skill can appreciate the scope and practice the present invention.

II. Sequestration of Carbon Dioxide Using Salts of Group II Metals

FIG. 1 depicts a simplified process-flow diagram illustrating general, exemplary embodiments of the apparatuses and methods of the present disclosure. This diagram is offered for illustrative purposes only, and thus it merely depicts specific embodiments of the present invention and is not intended to limit the scope of the claims in any way.

In the embodiment shown in **FIG. 1**, reactor **10** (*e.g.*, a road salt boiler) uses power, such as external power and/or recaptured power (*e.g.*, heat from hot flue gas or an external source of heat such as solar concentration or combustion), to drive a reaction represented by equation 1.



The water used in this reaction may be in the form of liquid, steam, a crystalline hydrate, *e.g.*, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, or it may be supercritical. In some embodiments, the reaction uses MgCl_2 to form $\text{Mg}(\text{OH})_2$ and/or $\text{Mg}(\text{OH})\text{Cl}$ (*see, e.g.*, **FIG. 2**). In some embodiments, the reaction uses CaCl_2 to form $\text{Ca}(\text{OH})_2$. Some or all of the Group 2 hydroxide or hydroxychloride (not shown) from equation 1 may be delivered to reactor **20**. In some embodiments, some or all of the Group 2 hydroxide and/or Group 2 hydroxychloride is delivered to reactor **20** as an aqueous solution. In some embodiments, some or all of the Group 2 hydroxide is delivered to reactor **20** in an aqueous suspension. In some embodiments, some or all of the Group 2 hydroxide is delivered to reactor **20** as a solid. In some embodiments, some or all of the hydrogen chloride (*e.g.*, in the form of vapor or in the form of hydrochloric acid) may be delivered to reactor **30** (*e.g.*, a rock melter). In some

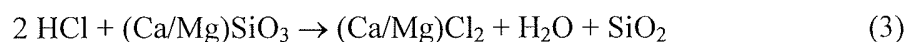
embodiments, the resulting Group 2 hydroxides are further heated to remove water and form corresponding Group 2 oxides. In some variants, some or all of these Group 2 oxides may then be delivered to reactor **20**.

Carbon dioxide from a source, *e.g.*, flue-gas, enters the process at reactor **20** (*e.g.*, a fluidized bed reactor, a spray-tower decarbonator or a decarbonation bubbler), potentially after initially exchanging waste-heat with a waste-heat/DC generation system. In some embodiments the temperature of the flue gas is at least 125 °C. The Group 2 hydroxide, some or all of which may be obtained from reactor **10**, reacts with carbon dioxide in reactor **20** according to the reaction represented by equation 2.



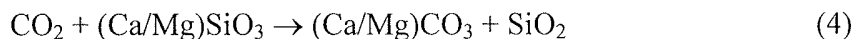
The water produced from this reaction may be delivered back to reactor **10**. The Group 2 carbonate is typically separated from the reaction mixture. Group 2 carbonates have a very low K_{sp} (solubility product constant). So they be separated as solids from other, more soluble compounds that can be kept in solution. In some embodiments, the reaction proceeds through Group 2 bicarbonate salts. In some embodiments, Group 2 bicarbonate salts are generated and optionally then separated from the reaction mixture. In some embodiments, Group 2 oxides, optionally together with or separately from the Group 2 hydroxides, are reacted with carbon dioxide to also form Group 2 carbonate salts. In some embodiments, the flue gas, from which CO₂ and/or other pollutants have been removed, is released to the air.

Group 2 silicates (*e.g.*, CaSiO₃, MgSiO₃, MgO·FeO·SiO₂, etc.) enter the process at reactor **30** (*e.g.*, a rock melter or a mineral dissociation reactor). In some embodiments, these Group 2 silicates are ground in a prior step. In some embodiments, the Group 2 silicates are inosilicates. These minerals may be reacted with hydrochloric acid, either as a gas or in the form of hydrochloric acid, some or all of which may be obtained from reactor **10**, to form the corresponding Group 2 metal chlorides (CaCl₂ and/or MgCl₂), water and sand (SiO₂). The reaction can be represented by equation 3.



Some or all of the water produced from this reaction may be delivered to reactor **10**. Some or all of the Group 2 chlorides from equation 3 may be delivered to reactor **20**. In some embodiments, some or all of the Group 2 chloride is delivered to reactor **20** as an aqueous solution. In some embodiments, some or all of the Group 2 chloride is delivered to reactor **20** in an aqueous suspension. In some embodiments, some or all of the Group 2 chloride is delivered to reactor **20** as a solid.

The net reaction capturing the summation of equations 1-3 is shown here as equation 4:



In another embodiment, the resulting $\text{Mg}_x\text{Ca}_{(1-x)}\text{CO}_3$ sequestrant is reacted with HCl in a manner to regenerate and concentrate the CO_2 . The Ca/MgCl_2 thus formed is returned to the decomposition reactor to produce CO_2 absorbing hydroxides or hydroxyhalides.

Through the process shown in **FIG. 1** and described herein, Group 2 carbonates are generated as end-sequestrant material from the captured CO_2 . Some or all of the water, hydrogen chloride and/or reaction energy may be cycled. In some embodiments, only some or none of these are cycled. In some embodiments, the water, hydrogen chloride and reaction energy made be used for other purposes.

In some embodiments, and depending on the concentration of CO_2 in the flue gas stream of a given plant, the methods disclosed herein may be used to capture 33-66% of the plant's CO_2 using heat-only as the driver (no electrical penalty). In some embodiments, the efficiencies of the methods disclosed herein improve with lower CO_2 -concentrations, and increase with higher (unscrubbed) flue-gas temperatures. For example, at 320 °C and 7% CO_2 concentration, 33% of flue-gas CO_2 can be mineralized from waste-heat alone. In other embodiments, *e.g.*, at the exit temperatures of natural gas turbines approximately 100% mineralization can be achieved.

These methods and devices can be further modified, *e.g.*, with modular components, optimized and scaled up using the principles and techniques of chemistry, chemical engineering, and/or materials science as applied by a person skilled in the art. Such principles and techniques are taught, for example, in U.S. Patent 7,727,374, U.S. Patent Application Publications 2006/0185985 and 2009/0127127, U.S. Patent Application No. 11/233,509, filed September 22, 2005, U.S. Provisional Patent Application No. 60/718,906, filed September 20, 2005; U.S. Provisional Patent Application No. 60/642,698, filed January 10, 2005; U.S. Provisional Patent Application No. 60/612,355, filed September 23, 2004, U.S. Patent Application No. 12/235,482, filed September 22, 2008, U.S. Provisional Application No. 60/973,948, filed September 20, 2007, U.S. Provisional Application No. 61/032,802, filed February 29, 2008, U.S. Provisional Application No. 61/033,298, filed March 3, 2008, U.S. Provisional Application No. 61/288,242, filed January 20, 2010, U.S. Provisional Application No. 61/362,607, filed July 8, 2010, and International Application No.

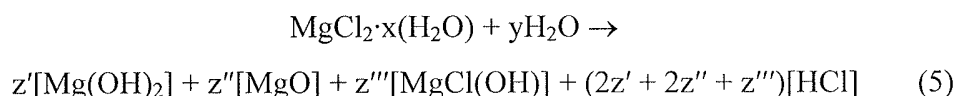
PCT/US08/77122, filed September 19, 2008. The entire text of each of the above-referenced disclosures (including any appendices) is specifically incorporated by reference herein.

The above examples were included to demonstrate particular embodiments of the invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

III. Sequestration of Carbon Dioxide Using Mg^{2+} as Catalyst

FIG. 2 depicts a simplified process-flow diagram illustrating general, exemplary embodiments of the apparatuses and methods of the present disclosure. This diagram is offered for illustrative purposes only, and thus it merely depicts specific embodiments of the present invention and is not intended to limit the scope of the claims in any way.

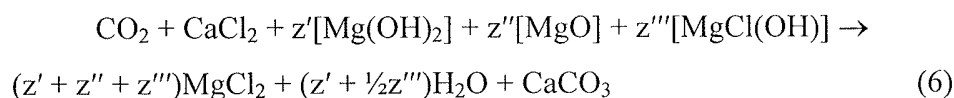
In the embodiment shown in **FIG. 2**, reactor **100** uses power, such as external power and/or recaptured power (*e.g.*, heat from hot flue gas), to drive a decomposition –type reaction represented by equation 5.



The water used in this reaction may be in the form of a hydrate of magnesium chloride, liquid, steam and/or it may be supercritical. In some embodiments, the reaction may occur in one, two, three or more reactors. In some embodiments, the reaction may occur as a batch, semi-batch or continuous process. In some embodiments, some or all of the magnesium salt product may be delivered to reactor **200**. In some embodiments, some or all of the magnesium salt product is delivered to reactor **200** as an aqueous solution. In some embodiments, some or all of the magnesium salt product is delivered to reactor **200** in an aqueous suspension. In some embodiments, some or all of the magnesium salt product is delivered to reactor **200** as a solid. In some embodiments, some or all of the hydrogen chloride (*e.g.*, in the form of vapor or in the form of hydrochloric acid) may be delivered to reactor **300** (*e.g.*, a rock melter). In some embodiments, the $Mg(OH)_2$ is further heated to remove water and form MgO . In some embodiments, the $MgCl(OH)$ is further heated to remove HCl and form MgO . In some variants, one or more of $Mg(OH)_2$, $MgCl(OH)$ and MgO may then be delivered to reactor **200**.

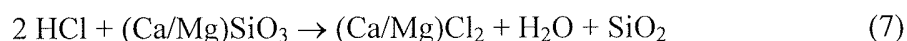
Carbon dioxide from a source, *e.g.*, flue-gas, enters the process at reactor **200** (*e.g.*, a fluidized bed reactor, a spray-tower decarbonator or a decarbonation bubbler), potentially

after initially exchanging waste-heat with a waste-heat/DC generation system. In some embodiments the temperature of the flue gas is at least 125 °C. Admixed with the carbon dioxide is the magnesium salt product from reactor **100** and CaCl₂ (e.g., rock salt). The carbon dioxide reacts with the magnesium salt product and CaCl₂ in reactor **200** according to the reaction represented by equation 6.



In some embodiments, the water produced from this reaction may be delivered back to reactor **100**. The calcium carbonate product (e.g., limestone, calcite) is typically separated (e.g., through precipitation) from the reaction mixture. In some embodiments, the reaction proceeds through magnesium carbonate and bicarbonate salts. In some embodiments, the reaction proceeds through calcium bicarbonate salts. In some embodiments, various Group 2 bicarbonate salts are generated and optionally then separated from the reaction mixture. In some embodiments, the flue gas, from which CO₂ and/or other pollutants have been removed, is released to the air, optionally after one or more further purification and/or treatment steps. In some embodiments, the MgCl₂ product, optionally hydrated, is returned to reactor **100**. In some embodiments, the MgCl₂ product is subjected to one or more isolation, purification and/or hydration steps before being returned to reactor **100**.

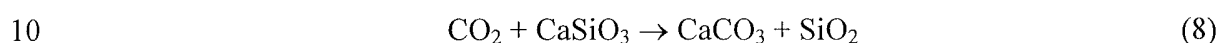
Calcium silicate (e.g., 3CaO·SiO₂, Ca₃SiO₅; 2CaO·SiO₂, Ca₂SiO₄; 3CaO·2SiO₂, Ca₃Si₂O₇ and CaO·SiO₂, CaSiO₃) enters the process at reactor **300** (e.g., a rock melter). In some embodiments, these Group 2 silicates are ground in a prior step. In some embodiments, the Group 2 silicates are inosilicates. In the embodiment of FIG. 2, the inosilicate is CaSiO₃ (e.g., wollastonite, which may itself, in some embodiments, contain small amounts of iron, magnesium and/or manganese substituting for iron). The CaSiO₃ is reacted with hydrogen chloride, either gas or in the form of hydrochloric acid, some or all of which may be obtained from reactor **100**, to form CaCl₂, water and sand (SiO₂). The reaction can be represented by equation 7.



Reaction	ΔH kJ/mole**	Reaction Temp. Range
2 HCl(g) + CaSiO ₃ → CaCl ₂ + H ₂ O + SiO ₂	-254	90 °C – 150 °C
2 HCl(g) + MgSiO ₃ → MgCl ₂ (aq) + H ₂ O + SiO ₂	-288	90 °C – 150 °C

** Enthalpies are based on reaction temperatures, and temperatures of incoming reactant and outgoing product streams. Some or all of the water produced from this reaction may be delivered to reactor **100**. Some or all of the CaCl_2 from equation 7 may be delivered to reactor **200**. In some embodiments, some or all of the CaCl_2 is delivered to reactor **200** as an aqueous solution. In some embodiments, some or all of the CaCl_2 is delivered to reactor **200** in an aqueous suspension. In some embodiments, some or all of the CaCl_2 is delivered to reactor **200** as a solid.

The net reaction capturing the summation of equations 5-7 is shown here as equation 8:



Reaction	ΔH kJ/mole**	ΔG kJ/mole**
$\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$	-89	-39

** Measured at standard temperature and pressure (STP). Through the process shown in **FIG. 2** and described herein, calcium carbonates are generated as end-sequestrant material from CO_2 and calcium inosilicate. Some or all of the various magnesium salts, water, hydrogen chloride and reaction energy may be cycled. In some embodiments, only some or none of these are cycled. In some embodiments, the water, hydrogen chloride and/or reaction energy made be used for other purposes.

These methods and devices can be further modified, optimized and scaled up using the principles and techniques of chemistry, chemical engineering, and/or materials science as applied by a person skilled in the art. Such principles and techniques are taught, for example, in U.S. Patent 7,727,374, U.S. Patent Application Publications 2006/0185985 and 2009/0127127, U.S. Patent Application No. 11/233,509, filed September 22, 2005, U.S. Provisional Patent Application No. 60/718,906, filed September 20, 2005; U.S. Provisional Patent Application No. 60/642,698, filed January 10, 2005; U.S. Provisional Patent Application No. 60/612,355, filed September 23, 2004, U.S. Patent Application No. 12/235,482, filed September 22, 2008, U.S. Provisional Application No. 60/973,948, filed September 20, 2007, U.S. Provisional Application No. 61/032,802, filed February 29, 2008, U.S. Provisional Application No. 61/033,298, filed March 3, 2008, U.S. Provisional Application No. 61/288,242, filed January 20, 2010, U.S. Provisional Application No. 61/362,607, filed July 8, 2010, and International Application No. PCT/US08/77122, filed

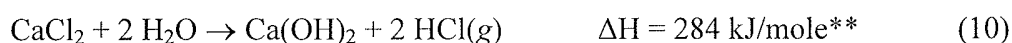
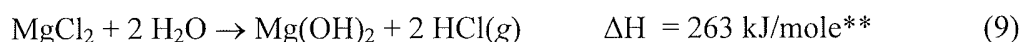
September 19, 2008. The entire text of each of the above-referenced disclosures (including any appendices) is specifically incorporated by reference herein.

The above examples were included to demonstrate particular embodiments of the invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

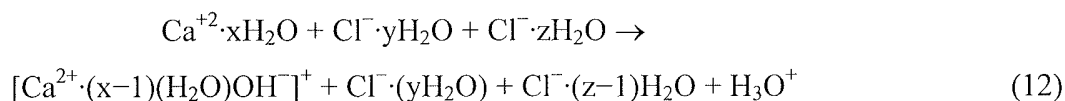
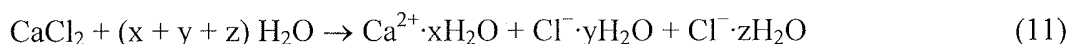
IV. Conversion of Group 2 Chlorides into Group 2 Hydroxides or Group II Hydroxy Chlorides

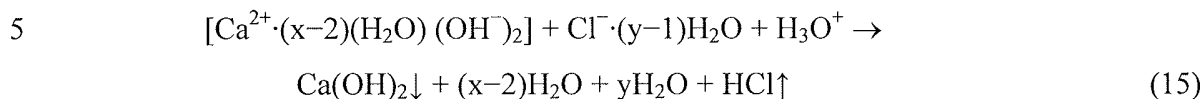
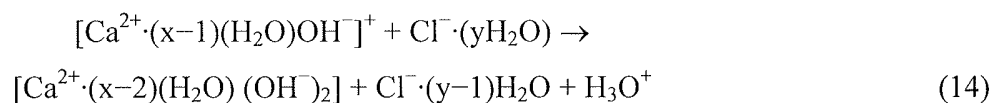
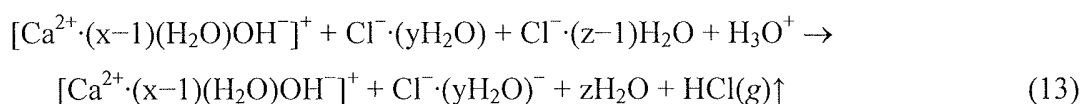
Disclosed herein are processes that react a Group 2 chloride, *e.g.*, CaCl_2 or MgCl_2 , with water to form a Group 2 hydroxide, a Group 2 oxide, and/or a mixed salt such as a Group 2 hydroxide chloride. Such reactions are typically referred to as decompositions. In some embodiments, the water may be in the form of liquid, steam, from a hydrate of the Group 2 chloride, and/or it may be supercritical. The steam may come from a heat exchanger whereby heat from an immensely combustible reaction, *i.e.* natural gas and oxygen or hydrogen and chlorine heats a stream of water. In some embodiments, steam may also be generated through the use of plant or factory waste heat. In some embodiments, the chloride salt, anhydrous or hydrated, is also heated.

In the case of Mg^{2+} and Ca^{2+} , the reactions may be represented by equations 9 and 10, respectively:



**Measured at 100 °C. The reactions are endothermic meaning energy, *e.g.*, heat has to be applied to make these reactions occur. Such energy may be obtained from the waste-heat generated from one or more of the exothermic process steps disclosed herein. The above reactions may occur according to one or more of the following steps:

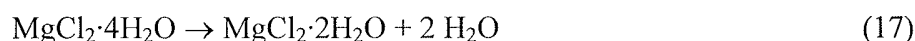
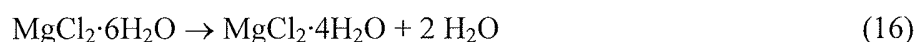




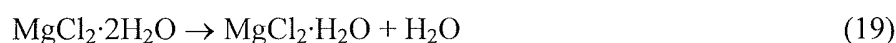
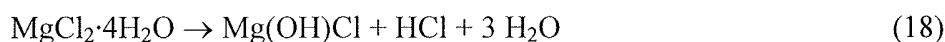
The reaction enthalpy (ΔH) for $\text{CaCl}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2 \text{HCl(g)}$ is 284 kJ/mole at 100 °C. In some variants, the salt $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, magnesium hexahydrate, is used. Since water is incorporated into the molecular structure of the salt, direct heating without any additional steam or water may be used to initiate the decomposition. Typical reactions

temperatures for the following reactions are shown here:

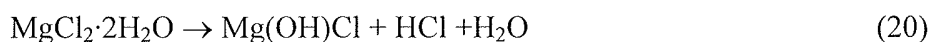
From 95-110 °C:



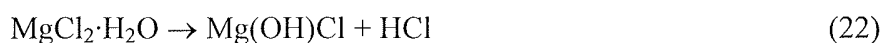
15 From 135-180 °C:



From 185-230 °C:



20 From >230 °C:

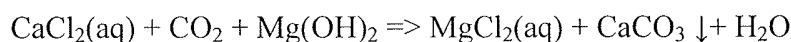


Reaction	Referenced Temp. Range	ΔH kJ/mole**	Temp. Reaction
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2 \text{H}_2\text{O}(g)$	95 °C – 110 °C	115.7	100°C
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2 \text{H}_2\text{O}(g)$	95 °C – 110 °C	134.4	100°C
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(g) + 3 \text{H}_2\text{O}(g)$	135 °C – 180 °C	275	160°C
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}(g)$	135 °C – 180 °C	70.1	160°C
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(g) + \text{H}_2\text{O}(g)$	185 °C – 230 °C	141	210°C
$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}(g)$	>230 °C	76.6	240°C
$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(g)$	>230 °C	70.9	240°C
$\text{Mg}(\text{OH})\text{Cl} \rightarrow \text{MgO} + \text{HCl}(g)$	>230 °C	99.2	450°C

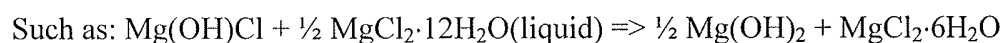
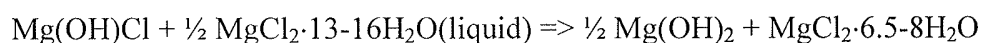
** ΔH values were calculated at the temperature of reaction (column “Temp. Reaction”). See the chemical reference Kirk Othmer 4th ed. Vol. 15 p. 343 1998 John Wiley and Sons, which is incorporated herein by reference. See example 1, below, providing results from a simulation that demonstrating the ability to capture CO₂ from flue gas using an inexpensive raw material, CaCl₂, to form CaCO₃. See also Energy Requirements and Equilibrium in the dehydration, hydrolysis and decomposition of Magnesium Chloride – K.K. Kelley, Bureau of Mines 1941 and Kinetic Analysis of Thermal Dehydration and Hydrolysis of MgCl₂·6H₂O by DTA and TG – Y. Kirsh, S. Yariv and S. Shoval – Journal of Thermal Analysis, Vol. 32 (1987), both of which are incorporated herein by reference in their entireties.

In certain aspects, Mg(OH)₂ can be more efficiently generated from MgCl₂ (via Mg(OH)Cl) by adjusting the proportion of MgCl₂ and water in the presence of Mg(OH)Cl. In order to optimize production of Mg(OH)₂, the amount of water in the chamber is adjusted to favor Mg(OH)₂ precipitation, while preventing formation of MgCl₂·6(H₂O) hydrates. Specifically, the amount of water in a Mg(OH)Cl solution is maintained at a water to MgCl₂ molar ratio of greater than or equal to 6, such as a ratio of between about 6 and 7. Under these conditions Mg(OH)₂, which is virtually insoluble, whereas the magnesium chloride remains in an aqueous solution. See, for example page 52 of de Bakker 2011, the entire disclosure of which is incorporated herein by reference.

Thus, to reach a product mixture of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ $\text{Mg}(\text{OH})\text{Cl}$ is reacted with an aqueous MgCl_2 solution, such as that from the bubble column. That reaction would be:



Boiling the mixture $\text{MgCl}_2 \cdot 13-16\text{H}_2\text{O}(\text{liquid}) + \Delta\text{H} \Rightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{solid}) + 7-9\text{H}_2\text{O}(\text{gas}) \uparrow$ would require significant energy usage. Thus, a solution more dilute than $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ shall cause the disproportionation of $\text{Mg}(\text{OH})\text{Cl}$, a solution of $\text{MgCl}_2 \cdot x\text{H}_2\text{O}(\text{liquid})$ where $x \geq 12$ should also be able to cause the disproportionation of $\text{Mg}(\text{OH})\text{Cl}$. The equation is written as follows:



The $\text{MgCl}_2(\text{aq})$ is being reconstituted to half of the original $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ by water removal and the remaining half of the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ forms from the disproportionation of $\text{Mg}(\text{OH})\text{Cl}$ by addition of water.

An example of a system that utilizes $\text{Mg}(\text{OH})_2$ generated as detailed above is shown in FIG. 38A-I. The Aspen diagram is below, and has a red rectangle around the defined “water disproportionator”. At the top of the red rectangle, $\text{Mg}(\text{OH})\text{Cl}$, stream SOLIDS-1, is leaving the decomposition reactor labeled “DECOMP”. Then in the module labeled MGOH2, the $\text{Mg}(\text{OH})\text{Cl}$ is mixed the aqueous MgCl_2 from the absorption column, stream RECYCLE2. They leave as a slurry from the unit as stream “4”, pass through a heat exchanger and send heat to the decomposition chamber. The stream is then named “13” which passes through a separation unit which separates the stream into stream MGCLSLRY ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ almost) and stream SOLIDS-2, which is the $\text{Mg}(\text{OH})_2$ heading to the absorption column.

V. Reaction of Group 2 Hydroxides and CO_2 to Form Group 2 Carbonates

In another aspect of the present disclosure, there are provided apparatuses and methods for the decarbonation of carbon dioxide sources using Group 2 hydroxides, Group 2 oxides, and/or Group 2 hydroxide chlorides as CO_2 adsorbents. In some embodiments, CO_2 is absorbed into an aqueous caustic mixture and/or solution where it reacts with the hydroxide and/or oxide salts to form carbonate and bicarbonate products. Sodium hydroxide, calcium hydroxide and magnesium hydroxide, in various concentrations, are known to readily absorb

CO₂. Thus, in embodiments of the present invention, Group 2 hydroxides, Group 2 oxides (such as CaO and/or MgO) and/or other hydroxides and oxides, *e.g.*, sodium hydroxide may be used as the absorbing reagent.

For example, a Group 2 hydroxide, *e.g.*, obtained from a Group 2 chloride, may be used in an adsorption tower to react with and thereby capture CO₂ based on one or both of the following reactions:



$$\Delta H = -117.92 \text{ kJ/mol}^{**}$$

$$\Delta G = -79.91 \text{ kJ/mol}^{**}$$



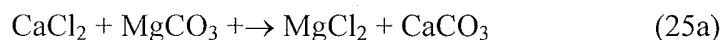
$$\Delta H = -58.85 \text{ kJ/mol}^{**}$$

$$\Delta G = -16.57 \text{ kJ/mol}^{**}$$

** Calculated at STP.

In some embodiments of the present invention, most or nearly all of the carbon dioxide is reacted in this manner. In some embodiments, the reaction may be driven to completion, for example, through the removal of water, whether through continuous or discontinuous processes, and/or by means of the precipitation of bicarbonate, carbonate, or a mixture of both types of salts. See example 1, below, providing a simulation demonstrating the ability to capture CO₂ from flue gas using an inexpensive raw material, Ca(CO)₂ derived from CaCl₂, to form CaCO₃.

In some embodiments, an initially formed Group 2 may undergo an salt exchange reaction with a second Group 2 hydroxide to transfer the carbonate anion. For example:



These methods and devices can be further modified, optimized and scaled up using the principles and techniques of chemistry, chemical engineering, and/or materials science as applied by a person skilled in the art. Such principles and techniques are taught, for example, in U.S. Patent 7,727,374, U.S. Patent Application No. 11/233,509, filed September 22, 2005, U.S. Provisional Patent Application No. 60/718,906, filed September 20, 2005; U.S. Provisional Patent Application No. 60/642,698, filed January 10, 2005; U.S. Provisional Patent Application No. 60/612,355, filed September 23, 2004, U.S. Patent Application No. 12/235,482, filed September 22, 2008, U.S. Provisional Application No. 60/973,948, filed September 20, 2007, U.S. Provisional Application No. 61/032,802, filed February 29, 2008,

U.S. Provisional Application No. 61/033,298, filed March 3, 2008, U.S. Provisional Application No. 61/288,242, filed January 20, 2010, U.S. Provisional Application No. 61/362,607, filed July 8, 2010, and International Application No. PCT/US08/77122, filed September 19, 2008. The entire text of each of the above-referenced disclosures (including
5 any appendices) is specifically incorporated by reference herein.

VI. Silicate Minerals for the Sequestration of Carbon Dioxide

In aspects of the present invention there are provided methods of sequestering carbon dioxide using silicate minerals. The silicate minerals make up one of the largest and most important classes of rock-forming minerals, constituting approximately 90 percent of the
10 crust of the Earth. They are classified based on the structure of their silicate group. Silicate minerals all contain silicon and oxygen. In some aspects of the present invention, Group 2 silicates may be used to accomplish the energy efficient sequestration of carbon dioxide.

In some embodiments, compositions comprising Group 2 inosilicates may be used. Inosilicates, or chain silicates, have interlocking chains of silicate tetrahedra with either SiO_3 ,
15 1:3 ratio, for single chains or Si_4O_{11} , 4:11 ratio, for double chains.

In some embodiments, the methods disclosed herein use compositions comprising Group 2 inosilicates from the pyroxene group. For example, enstatite (MgSiO_3) may be used.

In some embodiments, compositions comprising Group 2 inosilicates from the pyroxenoid group are used. For example, wollastonite (CaSiO_3) may be used. In some
20 embodiments, compositions comprising mixtures of Group 2 inosilicates may be employed, for example, mixtures of enstatite and wollastonite. In some embodiments, compositions comprising mixed-metal Group 2 inosilicates may be used, for example, diopside ($\text{CaMgSi}_2\text{O}_6$).

Wollastonite usually occurs as a common constituent of a thermally metamorphosed
25 impure limestone. Typically wollastonite results from the following reaction (equation 26) between calcite and silica with the loss of carbon dioxide:



In some embodiments, the present invention has the result of effectively reversing this natural process. Wollastonite may also be produced in a diffusion reaction in skarn. It develops
30 when limestone within a sandstone is metamorphosed by a dyke, which results in the formation of wollastonite in the sandstone as a result of outward migration of calcium ions.

In some embodiments, the purity of the Group 2 inosilicate compositions may vary. For example, it is contemplated that the Group 2 inosilicate compositions used in the disclosed processes may contain varying amounts of other compounds or minerals, including non-Group 2 metal ions. For example, wollastonite may itself contain small amounts of iron,
5 magnesium, and manganese substituting for calcium.

In some embodiments, compositions comprising olivine and/or serpentine may be used. CO₂ mineral sequestration processes utilizing these minerals have been attempted. The techniques of Goldberg *et al.* (2001) are incorporated herein by reference.

The mineral olivine is a magnesium iron silicate with the formula (Mg,Fe)₂SiO₄.
10 When in gem-quality, it is called peridot. Olivine occurs in both mafic and ultramafic igneous rocks and as a primary mineral in certain metamorphic rocks. Mg-rich olivine is known to crystallize from magma that is rich in magnesium and low in silica. Upon crystallization, the magma forms mafic rocks such as gabbro and basalt. Ultramafic rocks, such as peridotite and dunite, can be residues left after extraction of magmas and typically are
15 more enriched in olivine after extraction of partial melts. Olivine and high pressure structural variants constitute over 50% of the Earth's upper mantle, and olivine is one of the Earth's most common minerals by volume. The metamorphism of impure dolomite or other sedimentary rocks with high magnesium and low silica content also produces Mg-rich olivine, or forsterite.

20 VII. Generation of Group 2 Chlorides from Group 2 Silicates

Group 2 silicates, *e.g.*, CaSiO₃, MgSiO₃, and/or other silicates disclosed herein, may be reacted with hydrochloric acid, either as a gas or in the form of aqueous hydrochloric acid, to form the corresponding Group 2 metal chlorides (CaCl₂ and/or MgCl₂), water and sand. In some embodiments the HCl produced in equation 1 is used to regenerate the MgCl₂ and/or
25 CaCl₂ in equation 3. A process loop is thereby created. Table 1 below depicts some of the common calcium/magnesium containing silicate minerals that may be used, either alone or in combination. Initial tests by reacting olivine and serpentine with HCl have been successful. SiO₂ was observed to precipitate out and MgCl₂ and CaCl₂ were collected.

Table 1. Calcium/Magnesium Minerals.

Mineral	Formula (std. notation)	Formula (oxide notation)	Ratio Group 2:SiO ₂	Ratio Group 2: total
Olivine	(Mg,Fe) ₂ [SiO ₄]	(MgO,FeO) ₂ ·SiO ₂	1:1	1:2
Serpentine	Mg ₆ [OH] ₈ [Si ₄ O ₁₀]	6MgO·4SiO ₂ ·4H ₂ O	3:2	undefined
Sepiolite	Mg ₄ [(OH) ₂ Si ₆ O ₁₅][6H ₂ O]	3MgO·Mg(OH) ₂ ·6SiO ₂ ·6H ₂ O	2:3	undefined
Enstatite	Mg ₂ [Si ₂ O ₆]	2MgO·2SiO ₂	1:1	undefined
Diopside	CaMg[Si ₂ O ₆]	CaO·MgO·2SiO ₂	1:1	undefined
Tremolite	Ca ₂ Mg ₅ {[OH]Si ₄ O ₁₁ } ₂	2CaO·5MgO·8SiO ₂ ·H ₂ O	7:8	undefined
Wollastonite	CaSiO ₃	CaO·SiO ₂	1:1	undefined

See "Handbook of Rocks, Minerals & Gemstones by Walter Schumann Published 1993, Houghton Mifflin Co., Boston, New York, which is incorporated herein by reference.

VIII. Further Embodiments

In some embodiments, the conversion of carbon dioxide to mineral carbonates may be defined by two salts. The first salt is one that may be heated to decomposition until it becomes converted to a base (hydroxide and/or oxide) and emits an acid, for example, as a gas. This same base reacts with carbon dioxide to form a carbonate, bicarbonate or basic carbonate salt.

For example, in some embodiments, the present disclosure provides processes that react one or more salts from Tables A-C below with water to form a hydroxides, oxides, and/or a mixed hydroxide halides. Such reactions are typically referred to as decompositions.

In some embodiments, the water may be in the form of liquid, steam, and/or from a hydrate of the selected salt. The steam may come from a heat exchanger whereby heat from an immensely combustible reaction, *i.e.* natural gas and oxygen or hydrogen and chlorine heats a stream of water. In some embodiments, steam may also be generated through the use of plant or factory waste heat. In some embodiments, the halide salt, anhydrous or hydrated, is also heated.

Table A. Decomposition Salts

	Li^+		Na^+		K^+		Rb^+		Cs^+	
F^-	NC	N	4747	N	NC	N	10906	N	7490	N
Cl^-	3876	N	19497	N	8295	N	13616	N	7785	N
Br^-	3006	N	4336	N	9428	N	13814	N	8196	N
I^-	6110	N	6044	N	11859	N	9806	N	8196	N

Table B. Decomposition Salts (cont.)

	Mg^{+2}		Ca^{+2}		Sr^{+2}		Ba^{+2}	
F^-	4698	N	3433	N	10346	N	6143	N
Cl^-	4500*	6W*	5847	2W	9855	6W	8098	2W
Br^-	5010	6W	2743	N	10346	6W	8114	2W
I^-	2020	N	4960	N	9855	6W	10890	2W

*Subsequent tests have proven the heat of reaction within 1.5-4% of the thermodynamically derived value using TGA (thermogravimetric analysis) of heated samples and temperature ramp settings.

Table C. Decomposition Salts (cont.)

	Mn^{+2}		Fe^{+2}		Co^{+2}		Ni^{+2}		Zn^{+2}	
F^-	3318	N	2101	N	5847	N	5847	N	3285	N
Cl^-	5043	6W	3860	4W	3860	6W	4550	6W	8098	4W
Br^-	5256	6W	11925	4W	9855	6W	5010	6W	4418	4W
I^-	5043	6W	3055	4W	4123	6W	5831	6W	4271	4W
SO_4^{-2}	NC	4W	13485	4W	3351	4W	8985	6W	8344	7W

5

Table D. Decomposition Salts (cont.)

	Ag^+		La^{+3}	
F^-	2168	N	13255	7W
Cl^-	5486	N	7490	7W
Br^-	6242	N	5029	7W
I^-	6110	N	4813	7W
SO_4^{-2}	6159	N	10561	6W

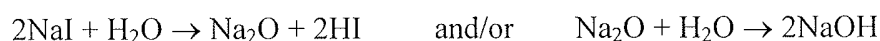
For Tables A-D, the numerical data corresponds to the energy per amount of CO_2 captured in kWh/tonne, NC = did not converge, and NA = data not available.

10 This same carbonate, bicarbonate or basic carbonate of the first salt reacts with a second salt to do a carbonate/bicarbonate exchange, such that the anion of second salt combines with the cation of the first salt and the cation of the second salt combines with the carbonate/bicarbonate ion of the first salt, which forms the final carbonate/bicarbonate.

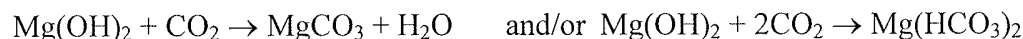
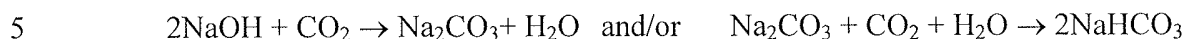
15 In some cases the hydroxide derived from the first salt is reacted with carbon dioxide and the second salt directly to form a carbonate/bicarbonate derived from (combined with the cation of) the second salt. In other cases the carbonate/bicarbonate/basic carbonate derived from (combined with the cation of) the first salt is removed from the reactor chamber and placed in a second chamber to react with the second salt. FIG. 27 shows an embodiment of this 2-salt process.

20 This reaction may be beneficial when making a carbonate/bicarbonate when a salt of the second metal is desired, and this second metal is not as capable of decomposing to form a CO_2 absorbing hydroxide, and if the carbonate/bicarbonate compound of the second salt is insoluble, i.e. it precipitates from solution. Below is a non-exhaustive list of examples of such reactions that may be used either alone or in combination, including in combination with one or more either reactions discussed herein.

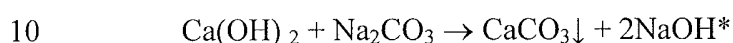
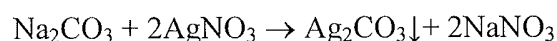
Examples for a Decomposition of a Salt-1:



Examples of a Decarbonation:



Examples of a Carbonate exchange with a Salt-2:



* In this instance the carbonate, Na_2CO_3 is Salt-2, and the salt decomposed to form Ca(OH)_2 , i.e. CaCl_2 is the Salt-1. This is the reverse of some of the previous examples in that the carbonate ion remains with Salt-1.

Known carbonate compounds include H_2CO_3 , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Rb_2CO_3 ,
 15 Cs_2CO_3 , BeCO_3 , MgCO_3 , CaCO_3 , SrCO_3 , BaCO_3 , MnCO_3 , FeCO_3 , CoCO_3 , CuCO_3 ,
 ZnCO_3 , Ag_2CO_3 , CdCO_3 , $\text{Al}_2(\text{CO}_3)_3$, Ti_2CO_3 , PbCO_3 , and $\text{La}_2(\text{CO}_3)_3$. Group IA elements are
 known to be stable bicarbonates, *e.g.*, LiHCO_3 , NaHCO_3 , RbHCO_3 , and CsHCO_3 . Group IIA
 and some other elements can also form bicarbonates, but in some cases, they may only be
 stable in solution. Typically rock-forming elements are H, C, O, F, Na, Mg, Al, Si, P, S, Cl,
 20 K, Ca, Ti, Mg and Fe. Salts of these that can be thermally decomposed into corresponding
 hydroxides by the least amount of energy per mole of CO_2 absorbing hydroxide may
 therefore be considered potential Salt-1 candidates.

Based on the energies calculated in Tables A-D, several salts have lower energies than
 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Table E below, summarizes these salts and the percent penalty reduction
 25 through their use relative to $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Table E: Section Lower Energy Alternative Salts

Compound	kw-hr/tonne	% reduction
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	4500	0%
LiCl	3876	16%
LiBr	3006	50%
NaBr	4336	4%
MgI_2	2020	123%
CaF_2	3433	31%

CaBr ₂	2743	64%
MnF ₂	3318	36%
FeF ₂	2102	114%
FeCl ₂ ·4H ₂ O	3860	17%
FeI ₂ ·4H ₂ O	3055	47%
CoCl ₂ ·6H ₂ O	3860	17%
CoI ₂ ·6H ₂ O	4123	9%
CoSO ₄ ·4H ₂ O	3351	34%
ZnF ₂ ·2H ₂ O	3285	37%
ZnBr ₂ ·4H ₂ O	4418	2%
ZnI ₂ ·4H ₂ O	4271	5%
CdF ₂	3137	43%
AgF	2168	108%

The following salts specify a decomposition reaction through their respective available MSDS information.

Table F.

Compound	Decomposition Energy	Notes
MgCl ₂ ·6H ₂ O	4500	
MnCl ₂ ·4H ₂ O	5043	only Mn ⁺² forms a stable carbonate
NaI·2H ₂ O	1023	too rare
CoI ₂ ·6H ₂ O	4123	too rare
FeCl ₂ ·4H ₂ O	3860	May oxidize to ferric oxide, this will not form a stable carbonate
LiBr	3006	too rare
Mg(NO ₃) ₂ ·4H ₂ O	1606	leaves NO _x
CoSO ₄ ·4H ₂ O	3351	somewhat rare leaves SO ₃
CdCl ₂ ·2.5H ₂ O	not avail.	toxic byproducts
Ca(NO ₃) ₂ ·4H ₂ O	2331	leaves NO ₂

Compound	References
MgCl ₂ ·6H ₂ O	
MnCl ₂ ·4H ₂ O	http://avogadro.chem.iastate.edu/MSDS/MnCl2.htm
NaI ₂ ·H ₂ O	http://www.chemicalbook.com/ProductMSDSDetailCB6170714_EN.htm
CoI ₂ ·6H ₂ O	http://www.espimetals.com/index.php/msds/527-cobalt-iodide
FeCl ₂ ·4H ₂ O	
LiBr	http://www.chemcas.com/material/cas/archive/7550-35-8_v1.asp
Mg(NO ₃) ₂ ·4H ₂ O	http://avogadro.chem.iastate.edu/MSDS/MgNO3-6H2O.htm

CoSO ₄ ·4H ₂ O	http://www.chemicalbook.com/ProductMSDSDetailCB0323842_EN.htm
CdCl ₂ ·2.5H ₂ O	http://www.espi Metals.com/index.php/msds/460-cadmium-chloride
Ca(NO ₃) ₂ ·4H ₂ O	http://avogadro.chem.iastate.edu/MSDS/Ca%28NO3%292-4H2O.htm

IX. Limestone Generation and Uses

In aspects of the present invention there are provided methods of sequestering carbon dioxide in the form of limestone. Limestone is a sedimentary rock composed largely of the mineral calcite (calcium carbonate: CaCO₃). This mineral has many uses, some of which are identified below.

Limestone in powder or pulverized form, as formed in some embodiments of the present invention, may be used as a soil conditioner (agricultural lime) to neutralize acidic soil conditions, thereby, for example, neutralizing the effects of acid rain in ecosystems. Upstream applications include using limestone as a reagent in desulfurizations.

Limestone is an important stone for masonry and architecture. One of its advantages is that it is relatively easy to cut into blocks or more elaborate carving. It is also long-lasting and stands up well to exposure. Limestone is a key ingredient of quicklime, mortar, cement, and concrete.

Calcium carbonate is also used as an additive for paper, plastics, paint, tiles, and other materials as both white pigment and an inexpensive filler. Purified forms of calcium carbonate may be used in toothpaste and added to bread and cereals as a source of calcium. CaCO₃ is also commonly used medicinally as an antacid.

Currently, the majority of calcium carbonate used in industry is extracted by mining or quarrying. By co-generating this mineral as part of carbon dioxide sequestration in some embodiments, this invention provides a non-extractive source of this important product.

X. Magnesium Carbonate Generation and Uses

In aspects of the present invention there are provided methods of sequestering carbon dioxide in the form of magnesium carbonate. Magnesium carbonate, MgCO₃, is a white solid that occurs in nature as a mineral. The most common magnesium carbonate forms are the anhydrous salt called magnesite (MgCO₃) and the di, tri, and pentahydrates known as barringtonite (MgCO₃·2H₂O), nesquehonite (MgCO₃·3H₂O), and lansfordite (MgCO₃·5H₂O), respectively. Magnesium carbonate has a variety of uses; some of these are briefly discussed below.

Magnesium carbonate may be used to produce magnesium metal and basic refractory bricks. MgCO_3 is also used in flooring, fireproofing, fire extinguishing compositions, cosmetics, dusting powder, and toothpaste. Other applications are as filler material, smoke suppressant in plastics, a reinforcing agent in neoprene rubber, a drying agent, a laxative, and for color retention in foods. In addition, high purity magnesium carbonate is used as antacid and as an additive in table salt to keep it free flowing.

Currently magnesium carbonate is typically obtained by mining the mineral magnesite. By co-generating this mineral as part of carbon dioxide sequestration in some embodiments, this invention provides a non-extractive source of this important product.

XI. Silicon Dioxide Generation and Uses

In aspects of the present invention there are provided methods of sequestering carbon dioxide that produce silicon dioxide as a byproduct. Silicon dioxide, also known as silica, is an oxide of silicon with a chemical formula of SiO_2 and is known for its hardness. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica is the most abundant mineral in the Earth's crust. This compound has many uses; some of these are briefly discussed below.

Silica is used primarily in the production of window glass, drinking glasses and bottled beverages. The majority of optical fibers for telecommunications are also made from silica. It is a primary raw material for many whiteware ceramics such as earthenware, stoneware and porcelain, as well as industrial Portland cement.

Silica is a common additive in the production of foods, where it is used primarily as a flow agent in powdered foods, or to absorb water in hygroscopic applications. In hydrated form, silica is used in toothpaste as a hard abrasive to remove tooth plaque. Silica is the primary component of diatomaceous earth which has many uses ranging from filtration to insect control. It is also the primary component of rice husk ash which is used, for example, in filtration and cement manufacturing.

Thin films of silica grown on silicon wafers *via* thermal oxidation methods can be quite beneficial in microelectronics, where they act as electric insulators with high chemical stability. In electrical applications, it can protect the silicon, store charge, block current, and even act as a controlled pathway to limit current flow.

Silica is typically manufactured in several forms including glass, crystal, gel, aerogel, fumed silica, and colloidal silica. By co-generating this mineral as part of carbon dioxide

sequestration in some embodiments, this invention provides another source of this important product.

XII. Separation of Products

Separation processes may be employed to separate carbonate and bicarbonate products from the liquid solution and/or reaction mixture. By manipulating the basic concentration, temperature, pressure, reactor size, fluid depth, and degree of carbonation, precipitates of one or more carbonate and/or bicarbonate salts may be caused to occur. Alternatively, carbonate/bicarbonate products may be separated from solution by the exchange of heat energy with incoming flue-gases.

The exit liquid streams, depending upon reactor design, may include water, CaCO_3 , MgCO_3 , $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{OH})_2$, NaOH , NaHCO_3 , Na_2CO_3 , and other dissolved gases in various equilibria. Dissolved trace emission components such as H_2SO_4 , HNO_3 , and Hg may also be found. In one embodiment, removing/separating the water from the carbonate product involves adding heat energy to evaporate water from the mixture, for example, using a reboiler. Alternatively, retaining a partial basic solution and subsequently heating the solution in a separating chamber may be used to cause relatively pure carbonate salts to precipitate into a holding tank and the remaining hydroxide salts to recirculate back to the reactor. In some embodiments, pure carbonate, pure bicarbonate, and mixtures of the two in equilibrium concentrations and/or in a slurry or concentrated form may then be periodically transported to a truck/tank-car. In some embodiments, the liquid streams may be displaced to evaporation tanks/fields where the liquid, such as water, may be carried off by evaporation.

The release of gaseous products includes a concern whether hydroxide or oxide salts will be released safely, *i.e.*, emitting “basic rain.” Emission of such aerosolized caustic salts may be prevented in some embodiments by using a simple and inexpensive condenser/reflux unit.

In some embodiments, the carbonate salt may be precipitated using methods that are used separately or together with a water removal process. Various carbonate salt equilibria have characteristic ranges where, when the temperature is raised, a given carbonate salt, *e.g.*, CaCO_3 will naturally precipitate and collect, which makes it amenable to be withdrawn as a slurry, with some fractional NaOH drawn off in the slurry.

XIII. Recovery of Waste-Heat

Because certain embodiments of the present invention are employed in the context of large emission of CO₂ in the form of flue-gas or other hot gases from combustion processes, such as those which occur at a power plant, there is ample opportunity to utilize this ‘waste’ heat, for example, for the conversion of Group 2 chlorides salts into Group 2 hydroxides. For instance, a typical incoming flue-gas temperature (after electro-static precipitation treatment, for instance) is approximately 300 °C. Heat exchangers can lower that flue-gas to a point less than 300°C, while warming the water and/or Group 2 chloride salt to facilitate this conversion.

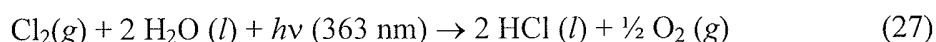
Generally, since the flue-gas that is available at power-plant exits at temperatures between 100°C (scrubbed typical), 300°C (after precipitation processing), and 900°C (precipitation entrance), or other such temperatures, considerable waste-heat processing can be extracted by cooling the incoming flue-gas through heat-exchange with a power-recovery cycle, for example an ammonia-water cycle (*e.g.*, a “Kalina” cycle), a steam cycle, or any such cycle that accomplishes the same thermodynamic means. Since some embodiments of the present invention rely upon DC power to accomplish the manufacture of the reagent/absorbent, the process can be directly powered, partially or wholly, by waste-heat recovery that is accomplished without the normal transformer losses associated with converting that DC power to AC power for other uses. Further, through the use of waste-heat-to-work engines, significant efficiencies can be accomplished without an electricity generation step being employed at all. In some conditions, these waste-heat recovery energy quantities may be found to entirely power embodiments of the present invention.

XIV. Alternative Processes

As noted above, some embodiments of the apparatuses and methods of the present disclosure produce a number of useful intermediates, by-products, and final products from the various reaction steps, including hydrogen chloride, Group 2 carbonate salts, Group 2 hydroxide salts, *etc.* In some embodiments, some or all of these may be used in one or more of the methods described below. In some embodiments, some or all of one of the starting materials or intermediates employed in one or more of the steps described above are obtained using one or more of the methods outlined below.

A. Use of Chlorine for the Chlorination of Group 2 Silicates

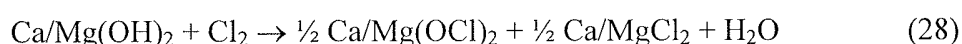
In some embodiments the chlorine gas may be liquefied to hydrochloric acid that is then used to chlorinate Group 2 silicate minerals. Liquefaction of chlorine and subsequent use of the hydrochloric acid is particularly attractive especially in situations where the chlorine market is saturated. Liquefaction of chlorine may be accomplished according to equation 27:



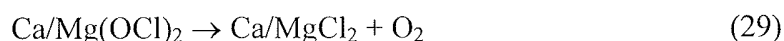
In some embodiments, the oxygen so produced may be returned to the air-inlet of the power plant itself, where it has been demonstrated throughout the course of power-industry investigations that enriched oxygen-inlet plants have (a) higher Carnot-efficiencies, (b) more concentrated CO₂ exit streams, (c) lower heat-exchange to warm inlet air, and (d) other advantages over non-oxygen-enhanced plants. In some embodiments, the oxygen may be utilized in a hydrogen/oxygen fuel cell. In some embodiments, the oxygen may serve as part of the oxidant in a turbine designed for natural gas power generation, for example, using a mixture of hydrogen and natural gas.

B. Use of Chlorine for the Chlorination of Group 2 Hydroxides

In some embodiments the chlorine gas may be reacted with a Group 2 hydroxide salts to yield a mixture of a chloride and a hypochlorite salts (equation 28). For example, HCl may be sold as a product and the Group 2 hydroxide salt may be used to remove excess chlorine.



The Group 2 hypochlorites may then be decomposed using a cobalt or nickel catalyst to form oxygen and the corresponding chloride (equation 29).



The calcium chloride and/or the magnesium chloride may then be recovered.

XV. Removal of other Pollutants from Source

In addition to removing CO₂ from the source, in some embodiments of the invention, the decarbonation conditions will also remove SO_x and NO_x and, to a lesser extent, mercury. In some embodiments of the present invention, the incidental scrubbing of NO_x, SO_x, and mercury compounds can assume greater economic importance; *i.e.*, by employing

embodiments of the present invention, coals that contain large amounts of these compounds can be combusted in the power plant with, in some embodiments, less resulting pollution than with higher-grade coals processed without the benefit of the CO₂ absorption process. Such principles and techniques are taught, for example, in U.S. Patent 7,727,374, U.S. Patent Application No. 11/233,509, filed September 22, 2005, U.S. Provisional Patent Application No. 60/718,906, filed September 20, 2005; U.S. Provisional Patent Application No. 60/642,698, filed January 10, 2005; U.S. Provisional Patent Application No. 60/612,355, filed September 23, 2004, U.S. Patent Application No. 12/235,482, filed September 22, 2008, U.S. Provisional Application No. 60/973,948, filed September 20, 2007, U.S. Provisional Application No. 61/032,802, filed February 29, 2008, U.S. Provisional Application No. 61/033,298, filed March 3, 2008, U.S. Provisional Application No. 61/288,242, filed January 20, 2010, U.S. Provisional Application No. 61/362,607, filed July 8, 2010, and International Application No. PCT/US08/77122, filed September 19, 2008. The entire text of each of the above-referenced disclosures (including any appendices) is specifically incorporated by reference herein.

XVI. Examples

The following examples are included to demonstrate some embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1 – Process Simulation of Capture CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.

One embodiment of the present invention was simulated using Aspen Plus v. 7.1 software using known reaction enthalpies, reaction free energies and defined parameters to determine mass and energy balances and suitable conditions for capturing CO₂ from a flue gas stream utilizing CaCl₂ and heat to form CaCO₃ product. These results show that it is possible to capture CO₂ from flue gas using inexpensive raw materials, CaCl₂ and water, to form CaCO₃.

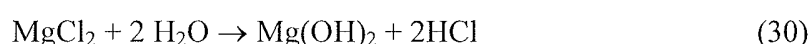
Part of the defined parameters includes the process flow diagram shown in FIG. 5. Results from the simulation suggest that it is efficient to recirculate an MgCl_2 stream to react with H_2O and heat to form Mg(OH)_2 . This Mg(OH)_2 then reacts with a saturated $\text{CaCl}_2/\text{H}_2\text{O}$ solution and CO_2 from the flue gas to form CaCO_3 , which is filtered out of the stream. The resulting MgCl_2 formed is recycled to the first reactor to begin the process again. This process is not limited to any particular source for CaCl_2 . For example, it may be obtained from reacting calcium silicate with HCl to yield CaCl_2 .

Constraints and parameters specified for this simulation include:

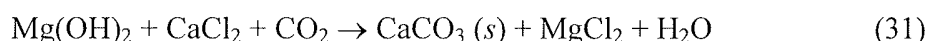
- The reactions were run at 100% efficiencies with no losses. The simulations can be modified when pilot runs determine the reaction efficiencies.
- Simulations did not account for impurities in the CaCl_2 feed stock or in any make-up MgCl_2 required due to losses from the system.

The results of this simulation indicate a preliminary net energy consumption of approximately 130 MM Btu/hr. Tables 2a and 2b provide mass and energy accounting for the various streams (the columns in the table) of the simulated process. Each stream corresponds to the stream of FIG. 5.

The process consists of two primary reaction sections and one solids filtration section. The first reactor heats $\text{MgCl}_2/\text{water}$ solution causing it to break down into a $\text{HCl}/\text{H}_2\text{O}$ vapor stream and a liquid stream of Mg(OH)_2 . The $\text{HCl}/\text{H}_2\text{O}$ vapor stream is sent to the HCl absorber column. The Mg(OH)_2 solution is sent to reactor 2 for further processing. The chemical reaction for this reactor can be represented by the following equation:



A CaCl_2 solution and a flue gas stream are added to the MgCl_2 in reactor 2. This reaction forms CaCO_3 , MgCl_2 and water. The CaCO_3 precipitates and is removed in a filter or decanter. The remaining MgCl_2 and water are recycled to the first reactor. Additional water is added to complete the water balance required by the first reactor. The chemical reaction for this reactor can be represented by the following equation:



The primary feeds to this process are CaCl_2 , flue gas (CO_2) and water. MgCl_2 in the system is used, reformed and recycled. The only MgCl_2 make-up required is to replace small amounts that leave the system with the CaCO_3 product, and small amounts that leave with the HCl/water product.

This process is a net energy user. There is cross heat exchange to recover the heat in high temperature streams to preheat the feed streams. Significant heat recovery may be obtained by reacting the concentrated HCl thus formed with silicate minerals.

Table 2a. Mass and Energy Accounting for Simulation of Capture CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Temperature F	485.8	151.6	250	95	77	95	104	77	536
Pressure psia	15	15	15	15	15	15	15	15	15
Vapor Frac	0	0	0.025	0	0		1	0	0
Mole Flow lbmol/hr	1594.401	7655.248	7653.691	3568.272	139.697	139.502	611.154	2220.337	1594.401
Mass Flow lb/hr	53195.71	162514.8	162514.8	115530.1	15504	13962.37	19206	40000	53195.71
Volume Flow gal/min	38.289	238.669	12389.12	114.43	14.159		30680.73	80.111	40.178
Enthalpy MMBtu/hr	-214.568	-918.028	-909.155	-574.405	-47.795		-27.903	-273.013	-205.695
H ₂ O	1473.175	105624.1	105603	33281.39			750.535	40000	1473.172
H ₂									
Cl ₂									
HCl	trace	trace	0.001	trace					trace
CO ₂		< 0.001	0.091	0.005			6158.236		
CO									
O ₂		0.055	0.055	0.055			2116.894		
N ₂		0.137	0.137	0.137			10180.34		
CaCl ₂					15504				
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		7.797	trace	7.797					
Mg ²⁺	11114.84	14507.52	14506.86	11942.37					11115.59
H ⁺	< 0.001	trace	trace	trace				trace	< 0.001
CaOH ⁺		< 0.001	trace	< 0.001					
MgOH ⁺	22.961	15.364	17.613	25.319					20.435

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				21433.25					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				13962.37		13962.37			
MgCO ₃ (s)		0.174							
CaCl ₂ -6W			42.623						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	8137.518	7.043	5.576	0.08					8139.306
ClO ⁻									
HCO ₃ ⁻		0.001	< 0.001	0.119					
Cl ⁻	32447.21	42352.6	42338.81	34877.24					32447.21
OH ⁻	< 0.001	0.001	0.001	< 0.001				< 0.001	< 0.001
CO ₃ ²⁻		trace	trace	0.001					
H ₂ O	0.028	0.65	0.65	0.288			0.039	1	0.028
H ₂									
Cl ₂									
HCl	trace	trace	3 PPB	trace					trace
CO ₂		trace	563 PPB	40 PPB			0.321		
CO									
O ₂		336 PPB	336 PPB	473 PPB			0.11		
N ₂		844 PPB	844 PPB	1 PPM			0.53		
CaCl ₂					1				
Ca(OH) ₂									
CaCO ₃									

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		48 PPM	trace	67 PPM					
Mg ²⁺	0.209	0.089	0.089	0.103					0.209
H ⁺	1 PPB	trace	trace	trace				trace	5 PPB
CAOH ⁺		1 PPB	trace	1 PPB					
MgOH ⁺	432 PPM	95 PPM	108 PPM	219 PPM					384 PPM
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				0.186					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				0.121		1			
MgCO ₃ (s)		1 PPM							
CaCl ₂ -6W			262 PPM						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	0.153	43 PPM	34 PPM	691 PPB					0.153
ClO ⁻									
HCO ₃ ⁻		5 PPB	trace	1 PPM					
Cl ⁻	0.61	0.261	0.261	0.302					0.61
OH ⁻	trace	6 PPB	6 PPB	trace				2 PPB	trace
CO ₃ ²⁻		trace	trace	12 PPB					

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
H ₂ O	81.774	5863.026	5861.857	1847.398			41.661	2220.337	81.773
H ₂									
Cl ₂									
HCl	trace	trace	< 0.001	trace					trace
CO ₂		trace	0.002	< 0.001			139.929		
CO									
O ₂		0.002	0.002	0.002			66.155		
N ₂		0.005	0.005	0.005			363.408		
CaCl ₂					139.697				
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		0.195	trace	0.195					
Mg ²⁺	457.328	596.922	596.894	491.376					457.358
H ⁺	< 0.001	trace	trace	trace				trace	< 0.001
CAOH ⁺		trace	trace	trace					
MgOH ⁺	0.556	0.372	0.426	0.613					0.495
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				105.426					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				139.502		139.502			
MgCO ₃ (s)		0.002							
CaCl ₂ -6W			0.195						

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	139.533	0.121	0.096	0.001					139.564
ClO ⁻									
HCO ₃ ⁻		< 0.001	trace	0.002					
Cl ⁻	915.211	1194.604	1194.215	983.753					915.211
OH ⁻	trace	< 0.001	< 0.001	trace				trace	trace
CO ₃ ²⁻		trace	trace	< 0.001					
H ₂ O	0.051	0.766	0.766	0.518			0.068	1	0.051
H ₂									
Cl ₂									
HCl	trace	trace	2 PPB	trace					trace
CO ₂		trace	271 PPB	29 PPB			0.229		
CO									
O ₂		223 PPB	223 PPB	478 PPB			0.108		
N ₂		640 PPB	640 PPB	1 PPM			0.595		
CaCl ₂					1				
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		25 PPM	trace	55 PPM					
Mg ²⁺	0.287	0.078	0.078	0.138					0.287
H ⁺	49 PPB	trace	trace	trace				2 PPB	156 PPB

Process Stream Names →	1	2	3	BOTTOMS	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
CaOH ⁺		trace	trace	trace					
MgOH ⁺	349 PPM	49 PPM	56 PPM	172 PPM					310 PPM
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				0.03					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				0.039		1			
MgCO ₃ (s)		269 PPB							
CaCl ₂ -6W			25 PPM						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	0.088	16 PPM	12 PPM	383 PPB					0.088
ClO ⁻									
HCO ₃ ⁻		2 PPB	trace	547 PPB					
Cl ⁻	0.574	0.156	0.156	0.276					0.574
OH ⁻	1 PPB	8 PPB	7 PPB	trace				2 PPB	1 PPB
CO ₃ ²⁻		trace	trace	6 PPB					
PH	5.319	6.955	5.875	7.557				6.999	5.152

Table 2b. Mass and Energy Accounting for Simulation of Capture CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
Temperature F	77	536	250	286.8	95	95
Pressure psia	15	15	15	15	15	15
Vapor Frac	0	1	0.025	0.021	0	1

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
Mole Flow lbmol/hr	3383.073	5781.846	7655.866	3814.738	3427.371	433.305
Mass Flow lb/hr	60947	109319.3	162515	93195.71	101567.8	12375.59
Volume Flow gal/min	122.063	512251.6	12240.14	5364.891	104.123	21428.56
Enthalpy MMBtu/hr	-415.984	-561.862	-909.177	-487.581	-502.044	-0.364
H ₂ O	60947	99124.11	105634.7	41473.17	33262.52	59.861
H ₂						
Cl ₂						
HCl		10195.18	0.087	0.009	trace	trace
CO ₂					trace	18.689
CO						
O ₂					0.055	2116.839
N ₂					0.137	10180.2
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					7.797	
Mg ²⁺			14519.48	11116.3	11938.09	
H ⁺	trace		< 0.001	trace	trace	
CaOH ⁺					< 0.001	
MgOH ⁺			0.112	17.999	25.309	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
MgCl ₂ -6W					21468.81	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					0.175	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				8141.025	0.024	
ClO ⁻						
HCO ₃ ⁻					trace	
Cl ⁻			42360.62	32447.2	34864.84	
OH ⁻	< 0.001		trace	< 0.001	< 0.001	
CO ₃ ²⁻					trace	
Mass Frac						
H ₂ O	1	0.907	0.65	0.445	0.327	0.005
H ₂						
Cl ₂						
HCl		0.093	534 PPB	92 PPB	trace	trace
CO ₂					trace	0.002
CO						
O ₂					538 PPB	0.171
N ₂					1 PPM	0.823
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					77 PPM	
Mg ²⁺			0.089	0.119	0.118	
H ⁺	trace		2 PPB	trace	trace	
CaOH ⁺					1 PPB	
MgOH ⁺			689 PPB	193 PPM	249 PPM	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					0.211	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					2 PPM	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				0.087	240 PPB	
ClO ⁻						
HCO ₃ ⁻					trace	
Cl ⁻			0.261	0.348	0.343	
OH ⁻	2 PPB		trace	2 PPB	trace	
CO ₃ ²⁻					trace	

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
H ₂ O	3383.073	5502.224	5863.617	2302.111	1846.35	3.323
H ₂						
Cl ₂						
HCl		279.622	0.002	< 0.001	trace	trace
CO ₂					trace	0.425
CO						
O ₂					0.002	66.154
N ₂					0.005	363.404
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					0.195	
Mg ²⁺			597.414	457.388	491.201	
H ⁺	trace		< 0.001	trace	trace	
CaOH ⁺					trace	
MgOH ⁺			0.003	0.436	0.613	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					105.601	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					0.002	

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				139.593	< 0.001	
ClO ⁻						
HCO ₃ ⁻					trace	
Cl ⁻			1194.83	915.211	983.403	
OH ⁻	trace		trace	trace	trace	
CO ₃ ²⁻					trace	
H ₂ O	1	0.952	0.766	0.603	0.539	0.008
H ₂						
Cl ₂						
HCl		0.048	311 PPB	62 PPB	trace	trace
CO ₂					trace	980 PPM
CO						
O ₂					498 PPB	0.153
N ₂					1 PPM	0.839
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					57 PPM	

Process Stream Names →	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	RETURN	RX3-VENT
Mg ²⁺			0.078	0.12	0.143	
H ⁺	2 PPB		43 PPB	trace	trace	
CaOH ⁺					trace	
MgOH ⁺			354 PPB	114 PPM	179 PPM	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					0.031	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					607 PPB	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				0.037	122 PPB	
ClO ⁻						
HCO ₃ ⁻					trace	
Cl ⁻			0.156	0.24	0.287	
OH ⁻	2 PPB		trace	2 PPB	trace	
CO ₃ ²⁻					trace	
PH	6.999		3.678	5.438	7.557	

**Example 2 (Case 1)– Process Simulation of Magnesium Ion Catalyzed
Capture CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.**

Results from the simulation suggest that it is efficient to heat a MgCl₂·6H₂O stream in three separate dehydration reactions, each in its own chamber, followed by a decomposition reaction, also in its own chamber, to form Mg(OH)Cl and HCl, i.e. total of four chambers. The Mg(OH)Cl is reacted with H₂O to form MgCl₂ and Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂·6H₂O formed is recycled along with the earlier product to the first reactor to begin the process again.

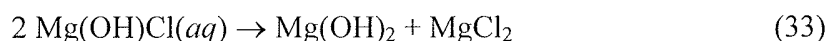
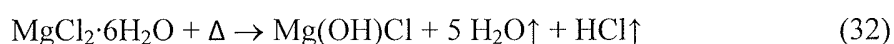
This process is not limited to any particular source for CaCl₂. For example, it may be obtained from reacting calcium silicate with HCl to yield CaCl₂.

Constraints and parameters specified for this simulation include:

- The reactions were run at 100% efficiencies with no losses. The simulations can be modified when pilot runs determine the reaction efficiencies.
- Simulations did not account for impurities in the CaCl₂ feed stock or in any make-up MgCl₂ required due to losses from the system.
- Part of the defined parameters include the process flow diagram shown in FIG. 6.

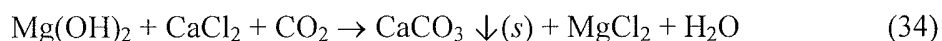
The results of this simulation indicate a preliminary net energy consumption of 5946 kwh/tonne CO₂. Table 3 provides mass and energy accounting for the various streams of the simulated process. Each stream corresponds to the stream of FIG. 6.

The process consists of two primary reactors and one solids filtration section. The first reactor heats MgCl₂·6H₂O causing it to break down into a HCl/H₂O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H₂O vapor stream is sent to a heat exchanger to recover extra heat. The Mg(OH)₂ formed from the Mg(OH)Cl is sent to reactor 2 for further processing. Chemical reaction(s) occurring in this reactor include the following:



A CaCl₂ solution and a flue gas stream are added to the Mg(OH)₂ in reactor 2. This reaction forms CaCO₃, MgCl₂ and water. The CaCO₃ precipitates and is removed in a filter or decanter. The remaining MgCl₂ and water are recycled to the first reactor. Additional

water is added to complete the water balance required by the first reactor. Chemical reaction(s) occurring in this reactor include the following:



The primary feeds to this process are CaCl_2 , flue gas (CO_2) and water. MgCl_2 in the system is used, reformed and recycled. The only MgCl_2 make-up required is to replace small amounts that leave the system with the CaCO_3 product, and small amounts that leave with the HCl/water product.

This process is a net energy user. The amount of energy is under investigation and optimization. There is cross heat exchange to recover the heat in high temperature streams to preheat the feed streams.

The steps for this process (Case 1) are summarized below:

CASE 1			
3 STEP Dehydration then Decomposition			
Hexahydrate is dehydrated in 3 separate chambers. Step 1 hex to tetra, Step 2 tetra to di, Step 3 di to mono. Monohydrate is decomposed into 80% Mg(OH)Cl 20% MgCl_2 in a fourth chamber.			
CO_2 Absorbed	53333	MTPY	
CaCl_2	134574	MTPY	
HCl Dry	88368	MTPY	
CaCO_3	105989	MTPY	
Hexahydrate recycled	597447	MTPY	
HEX TO TETRA (100 °C)	1757	kWh/tonne CO_2	
TETRA TO DI (125C °)	2135	kWh/tonne CO_2	
DI TO MONO (160 °C & HCl PP)	1150	kWh/tonne CO_2	
DECOMPOSITION (130 °C)	1051	kWh/tonne CO_2	
TO 80% Mg(OH)Cl 20% MgCl_2			
YIELDS 90% HCl VAPOR			
	0.9	MW	
Heat Recovery	148	kWh/tonne CO_2	
from 28% HCl vapor			
TOTAL	5946	kWh/tonne CO_2	

Table 3a. Mass and Energy Accounting for Case 1 Simulation.

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl VAPOR
Temperature C	25	95	104	25	100	125	160	130
Pressure psia	14.7	14.7	15.78	14.7	16.166	16.166	16.166	14.696
Mass VFrac	0	0	1	0	1	1	1	1
Mass SFrac	1	1	0	0	0	0	0	0
Mass Flow tonne/year	134573.943	121369.558	166332.6	290318.99	105883.496	105890.399	17179.526	97647.172
Volume Flow gal/min	30.929	22.514	76673.298	8099.644	82228.086	87740.919	10242.935	48861.42
Enthalpy MW	-30.599	-46.174	-17.479	-146.075	-44.628	-44.47	-3.258	-10.757
Density lb/cuft	136.522	169.146	0.068	1.125	0.04	0.038	0.053	0.063
H ₂ O	0	0	6499.971	290318.99	105883.496	105885.779	5681.299	9278.695
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	4.62	11498.227	88368.477
CO ₂	0	0	53333.098	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0	0
CaCl ₂	134573.943	80.499	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl VAPOR
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	1	1	0.331	0.095
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0.669	0.905
CO ₂	0	0	0.321	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0	0
N ₂	0	0	0.53	0	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	11.441	511.008	186.372	186.376	10	16.332
H ₂	0	0	0	0	0	0	0	0

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl VAPOR
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0.004	10	76.854
CO ₂	0	0	38.427	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0	0
N ₂	0	0	99.8	0	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0

Table 3b. Mass and Energy Accounting for Case 1 Simulation.

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	RECYCIE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
Temperature °C	125	100	104	95	95	95	160	130	160
Pressure psia	16.166	16.166	14.696	14.7	14.7	14.7	22.044	14.696	22.044
Mass V/Frac	0	0	0	0	1	0	0	0	1
Mass S/Frac	1	1	1	0.998	0	0.999	1	1	0
Mass Flow tonne/year	385672.688	491563.087	597446.583	598447.468	106499.178	719817.026	332737.843	235090.671	70114.371
Volume Flow gal/min	39.902	39.902	116.892	147.062	56469.408	167.321	39.902	43.473	42506.729
Enthalpy MW	-117.767	-175.272	-230.554	-231.312	0.241	-277.487	-88.626	-71.431	-25.379
Density lb/cuft	303.274	386.542	160.371	127.684	0.059	134.984	261.649	169.678	0.052
H ₂ O	0	0	0	1000	0	1000	0	0	58620.764
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0	11493.607
CO ₂	0	0	0	0	0.532	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0.165	18333.088	0.165	0	0	0
N ₂	0	0	0	0.72	88165.558	0.72	0	0	0
CaCl ₂	0	0	0	0	0	80.499	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	121289.059	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	49037.72	0
MgCl ₂ *W	0	0	0	0	0	0	332737.843	0	0
MgCl ₂ *2W	385662.96	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	491563.087	0	0	0	0	0	0	0

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	RECYCIE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
MgCl ₂ *6W	0	0	597446.583	597446.583	0	597446.583	0	0	0
Mg(OH)Cl	9.728	0	0	0	0	0	0	186052.951	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	0	0.002	0	0.001	0	0	0.836
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0	0.164
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0.172	0	0	0	0
N ₂	0	0	0	0	0.828	0	0	0	0
CaCl ₂	0	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0.168	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O) ₂ Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0.209	0
MgCl ₂ *W	0	0	0	0	0	0	1	0	0
MgCl ₂ *2W	1	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	1	0.998	0	0.83	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0.791	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
H ₂ O	0	0	0	1.76	0	1.76	0	0	103.182
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0	9.996
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	18.168	0	0	0	0
N ₂	0	0	0	0.001	99.799	0.001	0	0	0
CaCl ₂	0	0	0	0	0	0.023	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	38.427	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	16.332	0
MgCl ₂ *W	0	0	0	0	0	0	93.186	0	0
MgCl ₂ *2W	93.182	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	93.186	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	93.186	93.186	0	93.186	0	0	0
Mg(OH)Cl	0.004	0	0	0	0	0	0	76.854	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0

Example 3 – Process Simulation of Magnesium Ion Catalyzed Capture CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.

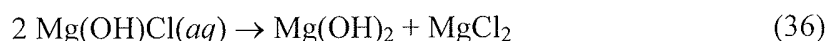
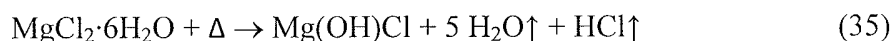
Part of the defined parameters includes the process flow diagram shown in FIG. 7. Results from the simulation suggest that it is efficient to heat a MgCl₂·6H₂O stream to form Mg(OH)Cl in two separate dehydration reactions, each in their own chambers followed by a decomposition reaction, also in its own chamber to form Mg(OH)Cl and HCl, i.e. a total of three chambers. The Mg(OH)Cl is reacted with H₂O to form MgCl₂ and Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂·6H₂O formed is recycled to the first reactor to begin the process again. This process is not limited to any particular source for CaCl₂. For example, it may be obtained from reacting calcium silicate with HCl to yield CaCl₂.

Constraints and parameters specified for this simulation include:

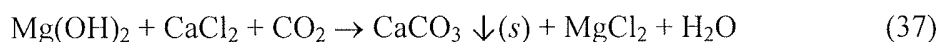
- The reactions were run at 100% efficiencies with no losses. The simulations can be modified when pilot runs determine the reaction efficiencies.
- Simulations did not account for impurities in the CaCl₂ feed stock or in any make-up MgCl₂ required due to losses from the system.

The results of this simulation indicate a preliminary net energy consumption of 4862 kwh/tonne CO₂. Table 4 provides mass and energy accounting for the various streams of the simulated process. Each stream corresponds to the stream in FIG. 7.

The process consists of two primary reactors and one solids filtration section. The first reactor heats MgCl₂·6H₂O causing it to break down into a HCl/H₂O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H₂O vapor stream is sent to a heat exchanger to recover extra heat. The Mg(OH)₂ formed from the Mg(OH)Cl is sent to reactor 2 for further processing. Chemical reaction(s) occurring in this reactor include the following:



A CaCl₂ solution and a flue gas stream are added to the Mg(OH)₂ in reactor 2. This reaction forms CaCO₃, MgCl₂ and water. The CaCO₃ precipitates and is removed in a filter or decanter. The remaining MgCl₂ and water are recycled to the first reactor. Additional water is added to complete the water balance required by the first reactor. Chemical reaction(s) occurring in this reactor include the following:



The primary feeds to this process are CaCl_2 , flue gas (CO_2) and water. MgCl_2 in the system is used, reformed and recycled. The only MgCl_2 make-up required is to replace small amounts that leave the system with the CaCO_3 product, and small amounts that leave with the

5 HCl/water product.

This process is a net energy user. The amount of energy is under investigation and optimization. There is cross heat exchange to recover the heat in high temperature streams to preheat the feed streams.

The steps for this process (Case 2) are summarized below:

CASE 2

2 STEP Dehydration then Decomposition

Hexahydrate is dehydrated in 2 separate chambers. Step 1 hex to tetra, Step 2 tetra to di. Di-hydrate is decomposed into 100% $\text{Mg}(\text{OH})\text{Cl}$.

CO_2 Absorbed	53333	MTPY
CaCl_2	134574	MTPY
HCl Dry	88368	MTPY
CaCO_3	105989	MTPY
Hexahydrate recycled	492737	MTPY
HEX TO TETRA (100 °C)	1445	kWh/tonne CO_2
TETRA TO DI (125 °C)	1774	kWh/tonne CO_2
DI-HYDRATE		
DEHYDRATION & DECOMPOSITION	1790	kWh/tonne CO_2
TO 100% $\text{Mg}(\text{OH})\text{Cl}$ (130 °C)		
YEILDS 66% HCl VAPOR		
NO CARRIER MgCl_2 = BETTER OVERALL EFFICIENCY		
NO USE OF HCl PP		
	0.9	
Heat Recovery	148	kWh/tonne CO_2
from 28% HCl vapor		
TOTAL	4862	kWh/tonne CO_2

Table 4a. Mass and Energy Accounting for Case 2 Simulation.

Process Stream Names →	5	7	8	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl Vapor
Temperature °C	98	114.1	101	25	95	40	25	100	125	130
Pressure psia	14.696	14.696	14.696	14.7	14.7	15.78	14.7	14.696	22.044	14.696
Mass VFrac	0	0	1	0	0	1	0	1	1	1
Mass SFrac	1	1	0	1	1	0	0	0	0	0
Mass Flow tonne/year	492736.693	405410.587	306683.742	134573.943	121369.558	166332.6	234646.82	87326.106	87329.947	132027.689
Volume Flow gal/min	96.405	32.909	224394.519	30.929	22.514	63660.018	6546.44	74598.258	53065.241	80593.954
Enthalpy MW	-190.292	-144.291	-98.931	-30.599	-46.174	-17.821	-118.063	-36.806	-36.675	-25.187
Density lb/cuft	160.371	386.542	0.043	136.522	169.146	0.082	1.125	0.037	0.052	0.051
H ₂ O	0	0	218315.265	0	0	6499.971	234646.82	87326.106	87326.106	43663.053
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0
HCl	0	0	88368.477	0	0	0	0	0	3.841	88364.636
CO ₂	0	0	0	0	0	53333.098	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18333.252	0	0	0	0
N ₂	0	0	0	0	0	88166.278	0	0	0	0
CaCl ₂	0	0	0	134573.943	80.499	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	121289.059	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	405410.587	0	0	0	0	0	0	0	0

Process Stream Names →	5	7	8	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl Vapor
MgCl ₂ *6W	492736.693	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.712	0	0	0.039	1	1	1	0.331
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0
HCl	0	0	0.288	0	0	0	0	0	0	0.669
CO ₂	0	0	0	0	0	0.321	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	0.11	0	0	0	0
N ₂	0	0	0	0	0	0.53	0	0	0	0
CaCl ₂	0	0	0	1	0.001	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0.999	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0	0	0
MgCl ₂ *6W	1	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	384.27	0	0	11.441	413.016	153.708	153.708	76.854

Process Stream Names →	5	7	8	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	H ₂ O-1	H ₂ O-2	HCl Vapor
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0
HCl	0	0	76.854	0	0	0	0	0	0.003	76.851
CO ₂	0	0	0	0	0	38.427	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18.168	0	0	0	0
N ₂	0	0	0	0	0	99.8	0	0	0	0
CaCl ₂	0	0	0	38.45	0.023	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	38.427	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	76.854	0	0	0	0	0	0	0	0
MgCl ₂ *6W	76.854	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0

Table 4b. Mass and Energy Accounting for Case 2 Simulation.

Process Stream Names →	LIQUID	MgCl ₂ -4W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
Temperature °C	94.9	100	75	95	95	95	125	130	118.1
Pressure psia	14.696	14.696	14.696	14.7	14.7	14.7	22.044	14.696	14.696
Mass VFrac	0.979	0	0	0	1	0	0	0	1

Process Stream Names →	LIQUID	MgCl ₂ -4W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
Mass SFrac	0	1	1	0.998	0	0.998	1	1	0
Mass Flow tonne/year	306683.742	405410.587	492736.693	493737.578	106499.178	615107.136	318080.64	186052.951	306683.742
Volume Flow gal/min	215496.035	32.909	96.405	126.575	56469.408	146.834	32.909	32.909	234621.606
Enthalpy MW	-99.487	-144.553	-190.849	-190.859	0.241	-237.034	-97.128	-61.083	-98.668
Density lb/cuft	0.045	386.542	160.371	122.394	0.059	131.442	303.277	177.393	0.041
H ₂ O	218315.265	0	0	1000	0	1000	0	0	218315.265
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	88368.477	0	0	0	0	0	0	0	88368.477
CO ₂	0	0	0	0	0.532	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0.165	18333.088	0.165	0	0	0
N ₂	0	0	0	0.72	88165.558	0.72	0	0	0
CaCl ₂	0	0	0	0	0	80.499	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	121289.059	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	318077.568	0	0
MgCl ₂ *4W	0	405410.587	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	492736.693	492736.693	0	492736.693	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	186052.951	0
Mg(OH) ₂	0	0	0	0	0	0	3.072	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0
Mass Frac									

Process Stream Names →	LIQUID	MgCl ₂ -4W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
H ₂ O	0.712	0	0	0.002	0	0.002	0	0	0.712
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0.288	0	0	0	0	0	0	0	0.288
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0.172	0	0	0	0
N ₂	0	0	0	0	0.828	0	0	0	0
CaCl ₂	0	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0.197	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	1	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	1	0.998	0	0.801	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	1	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0
H ₂ O	384.27	0	0	1.76	0	1.76	0	0	384.27
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	76.854	0	0	0	0	0	0	0	76.854
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0

Process Stream Names →	LIQUID	MgCl ₂ -4W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
O ₂	0	0	0	0	18.168	0	0	0	0
N ₂	0	0	0	0.001	99.799	0.001	0	0	0
CaCl ₂	0	0	0	0	0	0.023	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	38.427	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	76.852	0	0
MgCl ₂ *4W	0	76.854	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	76.854	76.854	0	76.854	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	76.854	0
Mg(OH) ₂	0	0	0	0	0	0	0.002	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0

**Example 4 – Process Simulation of Magnesium Ion Catalyzed Capture
CO₂ from Flue Gas Using CaCl₂ to Form CaCO₃.**

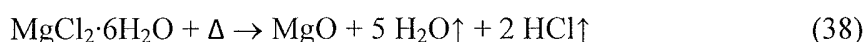
Part of the defined parameters include the process flow diagram shown in FIG. 8. Results from the simulation suggest that it is efficient to heat a MgCl₂·6H₂O stream to form MgO in a single chamber. The MgO is reacted with H₂O to form Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂·6H₂O formed is recycled to the first reactor to begin the process again. This process is not limited to any particular source for CaCl₂. For example, it may be obtained from reacting calcium silicate with HCl to yield CaCl₂.

Constraints and parameters specified for this simulation include:

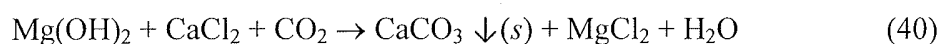
- The reactions were run at 100% efficiencies with no losses. The simulations can be modified when pilot runs determine the reaction efficiencies.
- Simulations did not account for impurities in the CaCl₂ feed stock or in any make-up MgCl₂ required due to losses from the system.

The results of this simulation indicate a preliminary net energy consumption of 3285 kwh/tonne CO₂. Table 5 provides mass and energy accounting for the various streams of the simulated process. Each stream corresponds to the stream of FIG. 8.

The process consists of two primary reactors and one solids filtration section. The first reactor heats MgCl₂·6H₂O causing it to break down into a HCl/H₂O vapor stream and a solid stream of MgO. The HCl/H₂O vapor stream is sent to a heat exchanger to recover extra heat. The Mg(OH)₂ formed from the MgO is sent to reactor 2 for further processing. Chemical reaction(s) occurring in this reactor include the following:



A CaCl₂ solution and a flue gas stream are added to the Mg(OH)₂ in reactor 2. This reaction forms CaCO₃, MgCl₂ and water. The CaCO₃ precipitates and is removed in a filter or decanter. The remaining MgCl₂ and water are recycled to the first reactor. Additional water is added to complete the water balance required by the first reactor. Chemical reaction(s) occurring in this reactor include the following::



The primary feeds to this process are CaCl₂, flue gas (CO₂) and water. MgCl₂ in the system is used, reformed and recycled. The only MgCl₂ make-up required is to replace small

amounts that leave the system with the CaCO_3 product, and small amounts that leave with the HCl/water product.

This process is a net energy user. The amount of energy is under investigation and optimization. There is cross heat exchange to recover the heat in high temperature streams to preheat the feed streams.

The steps for this process (Case 3) are summarized below:

CASE 3

Combined Dehydration/Decomposition to MgO

Hexahydrate is dehydrated and decomposed simultaneously at 450°C. Reactor yields 100% MgO .

CO_2 Absorbed	53333	MTPY
CaCl_2	134574	MTPY
HCl Dry	88368	MTPY
CaCO_3	105989	MTPY
Hexahydrate recycled	246368	MTPY
HEXAHYDRATE		
DEHYDRATION & DECOMPOSITION	3778	kWh/tonne CO_2
TO 100% MgO (450 °C)		
YIELDS 44.7% HCl VAPOR		
RECYCLES HALF AS MUCH HEXAHYDRATE		
BUT NEEDS HIGH QUALITY HEAT		
Heat Recovery	493	kWh/tonne CO_2
from 45% HCl vapor		
TOTAL	3285	kWh/tonne CO_2

Table 5a. Mass and Energy Accounting for Case 3 Simulation.

Process Stream Names →	CaCl ₂	CaCO ₃	FLUE GAS	H ₂ O	HCl VAP	MgCl ₂	MgCl ₂ -6W
Temperature °C	25	95	104	25	120	353.8	104
Pressure psia	14.7	14.7	15.78	14.7	14.696	14.7	14.7
Mass VFrac	0	0	1	0	1	0	0
Mass SFrac	1	1	0	0	0	1	1
Mass Flow tonne/year	134573.943	121369.558	166332.6	125489.188	197526.11	246368.347	246368.347
Volume Flow gal/min	30.929	22.514	76673.298	3501.038	137543.974	48.203	48.203
Enthalpy MW	-30.599	-46.174	-17.479	-63.14	-52.762	-92.049	-95.073
Density lb/cuft	136.522	169.146	0.068	1.125	0.045	160.371	160.371
H ₂ O	0	0	6499.971	125489.188	109157.633	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	88368.477	0	0
CO ₂	0	0	53333.098	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0
CaCl ₂	134573.943	80.499	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	246368.347	246368.347

Process Stream Names →	CaCl ₂	CaCO ₃	FLUE GAS	H ₂ O	HCl VAP	MgCl ₂	MgCl ₂ -6W
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	0.553	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	0.447	0	0
CO ₂	0	0	0.321	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0
N ₂	0	0	0.53	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	1	1
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
H ₂ O	0	0	11.441	220.881	192.135	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	76.854	0	0

Process Stream Names →	CaCl ₂	CaCO ₃	FLUE GAS	H ₂ O	HCl VAP	MgCl ₂	MgCl ₂ -6W
CO ₂	0	0	38.427	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0
N ₂	0	0	99.8	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	38.427	38.427
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0

Table 5b. Mass and Energy Accounting for Case 3 Simulation.

Process Stream Names →	Mg(OH)Cl1	Mg(OH)Cl2	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
Temperature °C	450	100	95	140	140	95	95	450	140
Pressure psia	14.696	14.696	14.7	14.7	14.7	14.7	14.7	14.696	14.7
Mass VFrac	0	0	0	0.004	0	1	0	1	1
Mass SFrac	1	1	0.996	0.996	1	0	0.997	0	0
Mass Flow tonne/year	48842.237	48842.237	247369.231	247369.231	246368.347	106499.178	368738.79	197526.11	1000.885
Volume Flow gal/min	6.851	6.851	78.372	994.232	48.203	56469.408	98.632	252994.849	946.03
Enthalpy MW	-22.38	-23	-95.676	-95.057	-94.638	0.241	-141.851	-49.738	-0.419

Process Stream Names →	Mg(OH)Cl1	Mg(OH)Cl2	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
Density lb/cuft	223.695	223.695	99.036	7.807	160.371	0.059	117.304	0.024	0.033
H ₂ O	0	0	1000	1000	0	0	1000	109157.633	1000
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	88368.477	0
CO ₂	0	0	0	0	0	0.532	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0.165	0.165	0	18333.088	0.165	0	0.165
N ₂	0	0	0.72	0.72	0	88165.558	0.72	0	0.72
CaCl ₂	0	0	0	0	0	0	80.499	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	121289.059	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	246368.347	246368.347	246368.347	0	246368.347	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	48842.237	48842.237	0	0	0	0	0	0	0
H ₂ O	0	0	0.004	0.004	0	0	0.003	0.553	0.999
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0.447	0
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0

Process Stream Names →	Mg(OH)Cl1	Mg(OH)Cl2	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
O ₂	0	0	0	0	0	0.172	0	0	0
N ₂	0	0	0	0	0	0.828	0	0	0.001
CaCl ₂	0	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	0.329	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0.996	0.996	1	0	0.668	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	1	1	0	0	0	0	0	0	0
H ₂ O	0	0	1.76	1.76	0	0	1.76	192.135	1.76
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	76.854	0
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18.168	0	0	0
N ₂	0	0	0.001	0.001	0	99.799	0.001	0	0.001
CaCl ₂	0	0	0	0	0	0	0.023	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	38.427	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0

Process Stream Names →	Mg(OH)Cl1	Mg(OH)Cl2	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	38.427	38.427	38.427	0	38.427	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	38.427	38.427	0	0	0	0	0	0	0

**Example 5 – Process Simulation of Magnesium Ion Catalyzed Capture
CO₂ from Flue Gas Using CaCl₂ to form CaCO₃.**

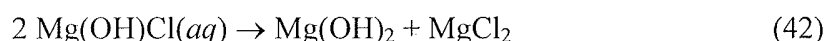
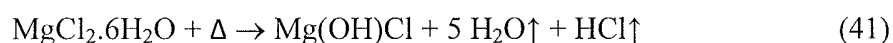
Part of the defined parameters include the process flow diagram shown in FIG. 9. Results from the simulation suggest that it is efficient to heat a MgCl₂·6H₂O stream to form Mg(OH)Cl in a single chamber. The Mg(OH)Cl is reacted with H₂O to form MgCl₂ and Mg(OH)₂, which then reacts with a saturated CaCl₂/H₂O solution and CO₂ from the flue gas to form CaCO₃, which is filtered out of the stream. The resulting MgCl₂·6H₂O formed is recycled to the first reactor to begin the process again. This process is not limited to any particular source for CaCl₂. For example, it may be obtained from reacting calcium silicate with HCl to yield CaCl₂.

Constraints and parameters specified for this simulation include:

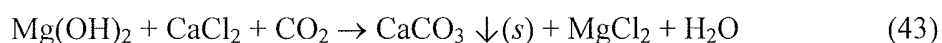
- The reactions were run at 100% efficiencies with no losses. The simulations can be modified when pilot runs determine the reaction efficiencies.
- Simulations did not account for impurities in the CaCl₂ feed stock or in any make-up MgCl₂ required due to losses from the system.

The results of this simulation indicate a preliminary net energy consumption of 4681 kwh/tonne CO₂. Table 6 provides mass and energy accounting for the various streams of the simulated process. Each stream corresponds to the stream of FIG. 9.

The process consists of two primary reactors and one solids filtration section. The first reactor heats MgCl₂·6H₂O causing it to break down into a HCl/H₂O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H₂O vapor stream is sent to a heat exchanger to recover extra heat. The Mg(OH)₂ formed from the Mg(OH)Cl is sent to reactor 2 for further processing. Chemical reaction(s) occurring in this reactor include the following:



A CaCl₂ solution and a flue gas stream are added to the Mg(OH)₂ in reactor 2. This reaction forms CaCO₃, MgCl₂ and water. The CaCO₃ precipitates and is removed in a filter or decanter. The remaining MgCl₂ and water are recycled to the first reactor. Additional water is added to complete the water balance required by the first reactor. Chemical reaction(s) occurring in this reactor include the following:



The primary feeds to this process are CaCl_2 , flue gas (CO_2) and water. MgCl_2 in the system is used, reformed and recycled. The only MgCl_2 make-up required is to replace small amounts that leave the system with the CaCO_3 product, and small amounts that leave with the HCl/water product.

- 5 This process is a net energy user. The amount of energy is under investigation and optimization. There is cross heat exchange to recover the heat in high temperature streams to preheat the feed streams.

The steps for this process (Case 4) are summarized below:

CASE 4

Combined Dehydration/Decomposition to $\text{Mg}(\text{OH})\text{Cl}$

Hexahydrate is dehydrated and decomposed simultaneously at 250 °C. Reactor yields 100% $\text{Mg}(\text{OH})\text{Cl}$.

CO_2 Absorbed	53333	MTPY
CaCl_2	134574	MTPY
HCl Dry	88368	MTPY
CaCO_3	105989	MTPY
Hexahydrate recycled	492737	MTPY
DEHYDRATION & DECOMPOSITION	5043	kWh/tonne CO_2
TO 100% $\text{Mg}(\text{OH})\text{Cl}$ (250 °C)		
YEILDS 28.8% HCl VAPOR		
	2.2	MW
Heat Recovery	361	kWh/tonne CO_2
from 28% HCl vapor		
TOTAL	4681	kWh/tonne CO_2

Table 6a. Mass and Energy Accounting for Case 4 Simulation.

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl1
Temperature °C	25	95	104	25	120	188	104	250
Pressure psia	14.7	14.7	15.78	14.7	14.696	14.7	14.7	14.696
Mass VFrac	0	0	1	0	1	0	0	0
Mass SFrac	1	1	0	0	0	1	1	1
Mass Flow tonne/year	134573.943	121369.558	166332.6	234646.82	306683.742	492736.693	492736.693	186052.951
Volume Flow gal/min	30.929	22.514	76673.298	6546.44	235789.67	96.405	96.405	32.909
Enthalpy MW	-30.599	-46.174	-17.479	-118.063	-98.638	-188.114	-190.147	-60.661
Density lb/cuft	136.522	169.146	0.068	1.125	0.041	160.371	160.371	177.393
H ₂ O	0	0	6499.971	234646.82	218315.265	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	88368.477	0	0	0
CO ₂	0	0	53333.098	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0	0
CaCl ₂	134573.943	80.499	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	492736.693	492736.693	0

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	HCIVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl1
Mg(OH)Cl	0	0	0	0	0	0	0	186052.951
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	0.712	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0.288	0	0	0
CO ₂	0	0	0.321	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0	0
N ₂	0	0	0.53	0	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	1	1	0
Mg(OH)Cl	0	0	0	0	0	0	0	1
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	0	11.441	413.016	384.27	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	76.854	0	0	0

Process Stream Names →	CaCl ₂	CaCO ₃	FLUEGAS	H ₂ O	HCIVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl1
CO ₂	0	0	38.427	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0	0
N ₂	0	0	99.8	0	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	76.854	76.854	0
Mg(OH)Cl	0	0	0	0	0	0	0	76.854
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0

Table 6b. Mass and Energy Accounting for Case 4 Simulation.

Process Stream Names →	Mg(OH)Cl ₂	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
Temperature °C	100	95	113.8	113.8	95	95	250	113.8
Pressure psia	14.696	14.7	14.7	14.7	14.7	14.7	14.696	14.7
Mass VFrac	0	0	0.002	0	1	0	1	1
Mass SFrac	1	0.998	0.998	1	0	0.998	0	0
Mass Flow tonne/year	186052.95	493737.58	493737.58	492736.69	106499.18	615107.14	306683.74	1000.89
Volume Flow gal/min	32.909	126.575	982.405	96.405	56469.408	146.834	313756.5	886
Enthalpy MW	-61.189	-190.859	-190.331	-189.91	0.241	-237.034	-96.605	-0.421

Process Stream Names →	Mg(OH)Cl ₂	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
Density lb/cuft	177.393	122.394	15.769	160.371	0.059	131.442	0.031	0.035
H ₂ O	0	1000	1000	0	0	1000	218315.27	1000
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	88368.477	0
CO ₂	0	0	0	0	0.532	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0.165	0.165	0	18333.088	0.165	0	0.165
N ₂	0	0.72	0.72	0	88165.558	0.72	0	0.72
CaCl ₂	0	0	0	0	0	80.499	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	121289.06	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	492736.69	492736.69	492736.69	0	492736.69	0	0
Mg(OH)Cl	186052.95	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	0.002	0.002	0	0	0.002	0.712	0.999
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0.288	0
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0

Process Stream Names →	Mg(OH)Cl ₂	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
O ₂	0	0	0	0	0.172	0	0	0
N ₂	0	0	0	0	0.828	0	0	0.001
CaCl ₂	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0.197	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0.998	0.998	1	0	0.801	0	0
Mg(OH)Cl	1	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	1.76	1.76	0	0	1.76	384.27	1.76
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	76.854	0
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	18.168	0	0	0
N ₂	0	0.001	0.001	0	99.799	0.001	0	0.001
CaCl ₂	0	0	0	0	0	0.023	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	38.427	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0

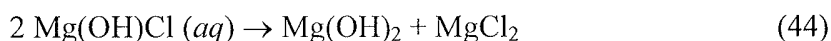
Process Stream Names →	Mg(OH)Cl ₂	RECYCLE1	RECYCLE2	RECYCLE3	RX2-VENT	SLURRY	VAPOR	VENT
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	76.854	76.854	76.854	0	76.854	0	0
Mg(OH)Cl	76.854	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0

Example 6 – Road Salt Boiler: Decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

FIG. 10 shows a graph of the mass percentage of a heated sample of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The sample's initial mass was approximately 70 mg and set at 100%. During the experiment, the sample's mass was measured while it was being thermally decomposed. The temperature was quickly ramped up to 150 °C, and then slowly increased by 0.5 °C per minute. At approximately 220 °C, the weight became constant, consistent with the formation of Mg(OH)Cl . The absence of further weight decrease indicated that almost all the water has been removed. Two different detailed decomposition mass analyses are shown in FIGS. 28 and 29, with the theoretical plateaus of different final materials shown. FIG. 30 confirms that MgO can be made by higher temperatures (here, 500 °C) than those which produce Mg(OH)Cl .

Example 7 – Dissolution of Mg(OH)Cl in H_2O

A sample of Mg(OH)Cl , produced by the heated decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, was dissolved in water and stirred for a period of time. Afterwards, the remaining precipitate was dried, collected and analyzed. By the formula of decomposition, the amount of Mg(OH)_2 could be compared to the expected amount and analyzed. The chemical reaction can be represented as follows:



The solubility data for Mg(OH)_2 and MgCl_2 is as follows:

MgCl_2 52.8 gm in 100 gm. H_2O (very soluble)
 Mg(OH)_2 0.0009 gm in 100 gm. H_2O (virtually insoluble)

Theoretical weight of recovered Mg(OH)_2 :

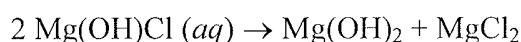
Given weight of sample: 3.0136 gm.

MW Mg(OH)Cl 76.764

MW Mg(OH)_2 58.32

Moles Mg(OH)_2 formed per mole $\text{Mg(OH)Cl} = \frac{1}{2}$

Expected amount of Mg(OH)_2



$$3.016 \text{ gm} * (\text{MW } \text{Mg(OH)}_2 \div (\text{MW } \text{Mg(OH)Cl} * \frac{1}{2}) = 1.1447 \text{ gm}$$

Precipitate collected = 1.1245 gm

% of theoretical collected = $(1.1447 \div 1.1245) * 100 = 98.24\%$

Analytical data:

Next the sample of $\text{Mg}(\text{OH})_2$ was sent for analysis, XRD (X-ray –diffraction) and EDS. Results are shown in FIG. 11. The top row of peaks is that of the sample, the spikes in the middle row are the signature of $\text{Mg}(\text{OH})_2$ while the spikes at the bottom are those of MgO . Thus verifying that the recovered precipitate from the dissolution of $\text{Mg}(\text{OH})\text{Cl}$ has a signal resembling that of $\text{Mg}(\text{OH})_2$.

Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
Mg-K	0.9472	1.014	96.88	96.02	+/-	0.23
Si-K	0.0073	2.737	1.74	1.99	+/-	0.17
Cl-K	0.0127	1.570	1.38	2.00	+/-	0.16
Total	100.00	100.00				

Note: Results do not include elements with $Z < 11$ (Na).

The EDS analysis reveals that very little chlorine [Cl] was incorporated into the precipitate. Note, this analysis cannot detect oxygen or hydrogen.

Example 8 – Decarbonation Bubbler Experiment: Production of CaCO_3 by reacting CO_2 with $\text{Mg}(\text{OH})_2$ {or $\text{Mg}(\text{OH})\text{Cl}$ } and CaCl_2

Approximately 20 grams of $\text{Mg}(\text{OH})_2$ was placed in a bubble column with two liters of water and CO_2 was bubbled through it for x minutes period of time. Afterwards some of the liquid was collected to which a solution of CaCl_2 was added. A precipitate immediately formed and was sent through the XRD and EDS. The chemical reaction can be represented as follows:



The XRD analysis (FIG. 12) coincides with the CaCO_3 signature.

EDS

Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
Mg-K	0.0070	2.211	2.52	1.55	+/-	0.10
Al-K	0.0013	1.750	0.33	0.22	+/-	0.04
Si-K	0.0006	1.382	0.12	0.09	+/-	0.03
Cl-K	0.0033	1.027	0.38	0.34	+/-	0.03
Ca-K	0.9731	1.005	96.64	97.80	+/-	0.30
Total	100.00	100.00				

Note: Results do not include elements with $Z < 11$ (Na).

The EDS analysis indicates almost pure CaCO_3 with only a 1.55% by weight magnesium impurity and almost no Chlorine from the CaCl_2 .

The same test was performed, except that $\text{Mg}(\text{OH})\text{Cl}$ from the decomposition of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was used instead of $\text{Mg}(\text{OH})_2$. Although $\text{Mg}(\text{OH})\text{Cl}$ has half the hydroxide $[\text{OH}^-]$, as $\text{Mg}(\text{OH})_2$ it is expected to absorb CO_2 and form precipitated CaCO_3 (PCC).

The XRD analysis (FIG. 13) coincides with the CaCO_3 signature.

5 EDS

Chi-sqd = 5.83 Livetime = 300.0 Sec.
Standardless Analysis

10 PROZA Correction Acc.Volt.= 20 kV Take-off Angle=35.00 deg
Number of Iterations = 3

Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
Mg-K	0.0041	2.224	1.48	0.90	+/-	0.09
S -K	0.0011	1.071	0.14	0.11	+/-	0.04
Ca-K	0.9874	1.003	98.38	98.98	+/-	0.34
Total	100.00	100.00				

20 Note: Results do not include elements with $Z < 11$ (Na).
Again the results indicate almost pure CaCO_3 , almost no Mg or Cl compounds.

Example 9A – Rock Melter Experiment: Reaction of Olivine and Serpentine with HCl

Samples of olivine $(\text{Mg},\text{Fe})_2\text{SiO}_4$ and serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ were crushed and
25 reacted with 6.1 molar HCl over a period of approximately 72 hours. Two sets of tests were
run, the first at room temperature and the second at 70 °C. These minerals have variable
formulae and often contain iron. After the samples were filtered, the resulting filtrand and
filtrate were dried in an oven overnight. The samples then went through XRD and EDS
analysis. The filtrates should have MgCl_2 present and the filtrand should be primarily SiO_2 .

30 Olivine Filtrate Reacted with HCl at Room Temperature

Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
Mg-K	0.1960	1.451	37.06	28.45	+/-	0.18
Si-K	0.0103	1.512	1.75	1.56	+/-	0.11
Cl-K	0.5643	1.169	58.89	65.94	+/-	0.31
Fe-K	0.0350	1.161	2.30	4.06	+/-	0.22
Total	100.00	100.00				

Olivine Filtrate Reacted with HCl at 70 °C

40 Note: Results do not include elements with $Z < 11$ (Na).
Element k-ratio ZAF Atom % Element Wt % Err.
(calc.) Wt % (1-Sigma)

Mg-K	0.1172	1.684	27.39	19.74	+/-	0.12
Si-K	0.0101	1.459	1.77	1.48	+/-	0.07
Cl-K	0.5864	1.142	63.70	66.94	+/-	0.24

45

Fe-K	0.0990	1.144	6.84	11.33	+/-	0.21
Ni-K	0.0045	1.128	0.29	0.51	+/-	0.09
Total	100.00	100.00				

5 Serpentine Filtrate Reacted with HCl at Room Temperature

Note: Results do not include elements with Z<11 (Na).

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
	Mg-K	0.1674	1.466	32.47	24.53	+/-	0.15
10	Al-K	0.0025	1.863	0.55	0.46	+/-	0.06
	Si-K	0.0033	1.456	0.55	0.48	+/-	0.04
	Cl-K	0.6203	1.141	64.22	70.77	+/-	0.27
	Ca-K	0.0016	1.334	0.17	0.21	+/-	0.05
	Cr-K	0.0026	1.200	0.19	0.31	+/-	0.07
15	Mn-K	0.0011	1.200	0.08	0.14	+/-	0.08
	Fe-K	0.0226	1.160	1.51	2.62	+/-	0.10
	Ni-K	0.0042	1.128	0.26	0.48	+/-	0.10
	Total	100.00	100.00				

20 Serpentine Filtrate Reacted with HCl at 70°C

Note: Results do not include elements with Z<11 (Na).

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
	Mg-K	0.1759	1.455	33.67	25.59	+/-	0.14
25	Al-K	0.0017	1.886	0.39	0.33	+/-	0.06
	Si-K	0.0087	1.468	1.46	1.28	+/-	0.04
	Cl-K	0.6014	1.152	62.46	69.27	+/-	0.25
	Cr-K	0.0016	1.199	0.12	0.19	+/-	0.06
	Fe-K	0.0268	1.161	1.78	3.11	+/-	0.17
30	Ni-K	0.0020	1.130	0.12	0.22	+/-	0.08
	Total	100.00	100.00				

Note: Results do not include elements with Z<11 (Na).

35 The filtrate clearly for both minerals serpentine and olivine at ambient conditions and 70 °C all illustrate the presence of MgCl₂, and a small amount of FeCl₂ in the case of olivine.

Olivine Filtrand Reacted with HCl at Room Temperature

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
40	Mg-K	0.2239	1.431	37.68	32.04	+/-	0.14
	Si-K	0.3269	1.622	53.96	53.02	+/-	0.19
	Cl-K	0.0140	1.658	1.87	2.32	+/-	0.06
	Cr-K	0.0090	1.160	0.58	1.05	+/-	0.08
	Mn-K	0.0013	1.195	0.08	0.16	+/-	0.09
45	Fe-K	0.0933	1.167	5.57	10.89	+/-	0.26
	Ni-K	0.0045	1.160	0.25	0.52	+/-	0.11
	Total	100.00	100.00				

Note: Results do not include elements with Z<11 (Na).

50

Olivine Filtrand Reacted with HCl at 70 °C

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
	Mg-K	0.2249	1.461	38.87	32.86	+/-	0.16

	Si-K	0.3030	1.649	51.12	49.94	+/- 0.21
	Cl-K	0.0223	1.638	2.96	3.65	+/- 0.14
	Ca-K	0.0033	1.220	0.29	0.41	+/- 0.05
	Cr-K	0.0066	1.158	0.42	0.76	+/- 0.08
5	Mn-K	0.0023	1.193	0.15	0.28	+/- 0.10
	Fe-K	0.0937	1.163	5.61	10.89	+/- 0.29
	Ni-K	0.0074	1.158	0.42	0.86	+/- 0.13
	Cu-K	0.0029	1.211	0.16	0.35	+/- 0.16
	Total	100.00	100.00			

10

Note: Results do not include elements with Z<11 (Na).

Given that the formula for olivine is $(\text{Mg,Fe})_2\text{SiO}_4$, and this is a magnesium rich olivine. The raw compound has a Mg:Si ratio of 2:1. However the filtrand, that which does not pass through the filter has a (Mg + Fe:Si) ratio of (37+5.5:52) or 0.817:1. (Atom % on

15 the chart), evidently more than 50% of the magnesium passed through the filter.

Serpentine Filtrand Reacted with HCl at Room Temperature

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
	Mg-K	0.1930	1.595	37.32	30.78	+/-	0.15
20	Si-K	0.2965	1.670	51.94	49.50	+/-	0.20
	Cl-K	0.0065	1.633	0.88	1.06	+/-	0.06
	Cr-K	0.0056	1.130	0.36	0.63	+/-	0.08
	Fe-K	0.1532	1.155	9.33	17.69	+/-	0.31
	Ni-K	0.0029	1.159	0.17	0.34	+/-	0.12
25	Total	100.00	100.00				

Note: Results do not include elements with Z<11 (Na).

Serpentine Filtrand Reacted with HCl at 70 °C

	Element (calc.)	k-ratio Wt %	ZAF (1-Sigma)	Atom %	Element	Wt %	Err.
30	Mg-K	0.1812	1.536	33.53	27.83	+/-	0.13
	Si-K	0.3401	1.593	56.49	54.18	+/-	0.18
	Cl-K	0.0106	1.651	1.45	1.75	+/-	0.11
35	Cr-K	0.0037	1.142	0.24	0.43	+/-	0.07
	Mn-K	0.0009	1.188	0.05	0.10	+/-	0.08
	Fe-K	0.1324	1.159	8.05	15.35	+/-	0.26
	Ni-K	0.0032	1.160	0.18	0.37	+/-	0.11
40	Total	100.00	100.00				

Note: Results do not include elements with Z<11 (Na).

Given that the formula of serpentine is $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ the initial 1.5:1 ratio of (Mg + Fe) to Si has been whittled down to $(37 + 9.3:56.5) = 0.898:1$.

45 Example 9B – Temperature/Pressure Simulation for Decomposition of $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$

Pressure and temperature was varied, as shown below (Table 7) and in FIG. 14, to determine the effect this has on the equilibrium of the decomposition of $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$.

Inputs are:

- 1) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- 5 2) CaCl_2
- 3) The temperature of the hot stream leaving the heat exchanger (HX) labeled $\text{Mg}(\text{OH})\text{Cl}$ (see FIGS. 7-8).
- 4) Percentage of Solids separated in decanter.
- 5) Water needed labeled H_2O
- 10 6) Flue Gas.

Table 7.

VARY 1	VARY 2	INPUT	Mg(OH)Cl	MgO	Q	
REACTOR1	REACTOR1					
PARAM	PARAM					
TEMP	PRES					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/tonne CO2
400	5	51.08399	25.31399	25.77001	23.63765	3883
410	5	38.427	0	38.427	19.85614	3261
420	5	38.427	0	38.427	19.87482	3264
430	5	38.427	0	38.427	19.89354	3268
440	5	38.427	0	38.427	19.9123	3271
450	5	38.427	0	38.427	19.93111	3274
400	7	76.854	76.854	0	31.37484	5153
410	7	53.24627	29.63854	23.60773	24.31186	3993
420	7	38.427	0	38.427	19.87482	3264
430	7	38.427	0	38.427	19.89354	3268
440	7	38.427	0	38.427	19.9123	3271
450	7	38.427	0	38.427	19.93111	3274
400	9	76.854	76.854	0	31.37484	5153
410	9	72.85115	68.84829	4.002853	30.20646	4961
420	9	50.2148	23.5756	26.6392	23.42411	3847
430	9	38.427	0	38.427	19.89354	3268
440	9	38.427	0	38.427	19.9123	3271
450	9	38.427	0	38.427	19.93111	3274
400	11	76.854	76.854	0	31.37484	5153
410	11	76.854	76.854	0	31.41	5159
420	11	64.78938	52.72476	12.06462	27.81251	4568
430	11	44.67748	12.50096	32.17652	21.77822	3577
440	11	38.427	0	38.427	19.9123	3271
450	11	38.427	0	38.427	19.93111	3274
400	13	76.854	76.854	0	31.37484	5153

VARY 1	VARY 2	INPUT	Mg(OH)Cl	MgO	Q	
REACTOR1	REACTOR1					
PARAM	PARAM					
TEMP	PRES					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/tonne CO2
410	13	76.854	76.854	0	31.41	5159
420	13	76.854	76.854	0	31.44515	5165
430	13	55.59535	34.3367	21.25865	25.07026	4118
440	13	38.427	0	38.427	19.9123	3271
450	13	38.427	0	38.427	19.93111	3274
400	15	76.854	76.854	0	31.37484	5153
410	15	76.854	76.854	0	31.41	5159
420	15	76.854	76.854	0	31.44515	5165
430	15	66.51322	56.17244	10.34078	28.36229	4659
440	15	46.41875	15.98351	30.43525	22.32544	3667
450	15	38.427	0	38.427	19.93111	3274
200	5	127	76.854	0	47.51946	7805
210	5	85	76.854	0	33.34109	5476
220	5	77	76.854	0	30.74184	5049
230	5	77	76.854	0	30.77702	5055
240	5	77	76.854	0	30.8122	5061
250	5	77	76.854	0	30.84739	5067
200	7	184	76.854	0	66.57309	10935
210	7	125	76.854	0	46.75184	7679
220	7	85	76.854	0	33.32609	5474
230	7	77	76.854	0	30.777	5055
240	7	77	76.854	0	30.81218	5061
250	7	77	76.854	0	30.84737	5067
200	9	297	76.854	0	89.51079	14702
210	9	165	76.854	0	60.16258	9882
220	9	113	76.854	0	42.92123	7050
230	9	78	76.854	0	31.04401	5099
240	9	77	76.854	0	30.81217	5061
250	9	77	76.854	0	30.84735	5067
200	11	473	76.854	0	136.5784	22433
210	11	205	76.854	0	73.57332	12084
220	11	142	76.854	0	52.51638	8626
230	11	98	76.854	0	38.01558	6244
240	11	77	76.854	0	30.81216	5061
250	11	77	76.854	0	30.84734	5067
200	13	684	76.854	0	192.9858	31698
210	13	303	76.854	0	91.43505	15018
220	13	170	76.854	0	62.11152	10202
230	13	119	76.854	0	44.98715	7389

VARY 1	VARY 2	INPUT	Mg(OH)Cl	MgO	Q	
REACTOR1	REACTOR1					
PARAM	PARAM					
TEMP	PRES					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/tonne CO2
240	13	83.3323	76.854	0	33.00459	5421
250	13	76.854	76.854	0	30.84733	5067
200	15	930.5287	76.854	0	258.7607	42502
210	15	422.9236	76.854	0	123.7223	20322
220	15	198.7291	76.854	0	71.70666	11778
230	15	139.6567	76.854	0	51.95871	8534
240	15	98.51739	76.854	0	38.14363	6265
250	15	76.854	76.854	0	30.84733	5067

Examples 10 – 21

The following remaining examples are concerned with obtaining the necessary heat to perform the decomposition reaction using waste heat emissions from either coal or natural gas power plants. In order to obtain the necessary heat from coal flue gas emissions, the heat source may be located prior to the baghouse where the temperature ranges from 320-480 °C in lieu of the air pre-heater. See Reference: pages 11-15 of “The structural design of air and gas ducts for power stations and industrial Boiler Applications,” Publisher: American Society of Civil Engineers (August 1995), which is incorporated by reference herein in its entirety.

Open cycle natural gas plants have much higher exhaust temperatures of 600 °C. See Reference: pages 11-15 of “The structural design of air and gas ducts for power stations and industrial Boiler Applications,” Publisher: American Society of Civil Engineers (August 1995), which is incorporated by reference herein in its entirety. Additionally, the decomposition reaction of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ may also run in two different modes, complete decomposition to MgO or a partial decomposition to Mg(OH)Cl. The partial decomposition to Mg(OH)Cl requires in some embodiments a temperature greater than 180 °C whereas the total decomposition to MgO requires in some embodiments a temperature of 440 °C or greater.

Additionally the incoming feed to the process can be represented as a continuum between 100% Calcium Silicate (CaSiO_3) and 100% Magnesium Silicate (MgSiO_3) with Diopside ($\text{MgCa}(\text{SiO}_3)_2$) (or a mixture of CaSiO_3 and MgSiO_3 in a 1:1 molar ratio) representing an intermediate 50% case. For each of these cases the resulting output will range in some embodiments from calcium carbonate (CaCO_3) to magnesium carbonate

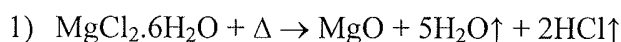
(MgCO₃) with Dolomite CaMg(CO₃)₂ representing the intermediate case. The process using 100% calcium silicate is the Ca-Mg process used in all of the previously modeled embodiments. It is also important to note that the 100% magnesium silicate process uses no calcium compounds; whereas the 100% calcium silicate incoming feed process does use magnesium compounds, but in a recycle loop, only makeup magnesium compounds are required.

Further details regarding the Ca-Mg, Mg only, Diopside processes, for example, using complete and partial decomposition of hydrated MgCl₂ to MgO and Mg(OH)Cl, respectively, are depicted below.

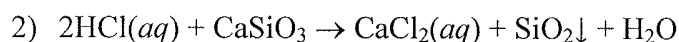
10 I) Ca-Mg Process

Overall reaction $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$

a) Full decomposition (“the CaSiO₃-MgO process”):

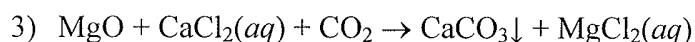


A thermal decomposition reaction.

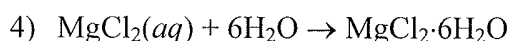


A rock melting reaction.

Note 5 H₂O will be present per 2 moles of HCl during the reaction.

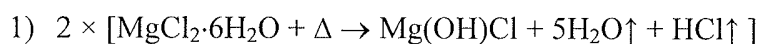


Some versions of this equation use Mg(OH)₂ which is formed from MgO and H₂O.



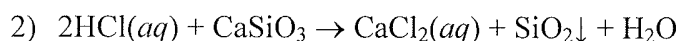
Regeneration of MgCl₂·6H₂O, return to #1.

b) Partial decomposition (“the CaSiO₃-Mg(OH)Cl process”):

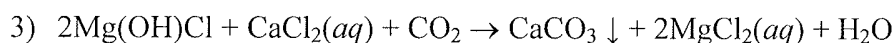


Thermal decomposition.

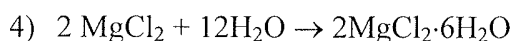
Twice as much MgCl₂·6H₂O is needed to trap the same amount of CO₂.



Rock melting reaction.



CO₂ capture reaction

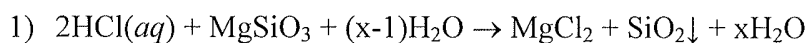


Regeneration of MgCl₂·6H₂O, return to #1.

II) Mg Only Process

Overall reaction $\text{MgSiO}_3 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{SiO}_2$

c) Full decomposition (“the MgSiO_3 - MgO process”)



Rock melting reaction.



Thermal decomposition reaction.

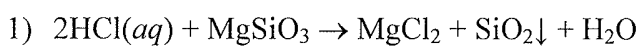
Note “x-1” moles H_2O will be produced per 2 moles of HCl .



CO_2 capture reaction.

Note, in this embodiment no recycle of MgCl_2 is required. The value of x, the number of waters of hydration is much lower than 6 because the MgCl_2 from the rock melting reaction is hot enough to drive much of the water into the vapor phase. Therefore the path from the rock melting runs at steady state with “x” as modeled with a value of approximately 2.

d) Partial decomposition (“the MgSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ process”)



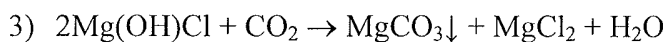
Rock melting reaction.

Note “x-1” H_2O will be present per mole of HCl during the reaction.

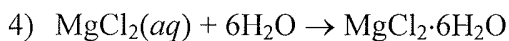


Decomposition.

Twice as much $\text{MgCl}_2 \cdot (x-1)\text{H}_2\text{O}$ is needed to trap the same amount of CO_2 .



CO_2 capture reaction.



Regenerate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Return to #1.

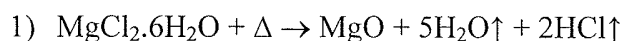
Note, in this embodiment half of the MgCl_2 is recycled. The value of x, the number of waters of hydration is somewhat lower than 6 because half of the MgCl_2 is from the rock melting reaction which is hot enough to drive much of the water into the vapor phase and the remaining half is recycled from the absorption column. Therefore the number of hydrations for the total amount of MgCl_2 at steady state will have a value of approximately 4, being the average between the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$.

III) Diopside or Mixed process:

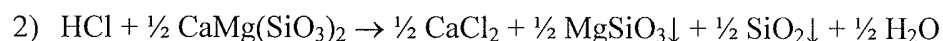
Note diopside is a mixed calcium and magnesium silicate and dolomite is a mixed calcium and magnesium carbonate.

Overall reaction: $\frac{1}{2} \text{CaMg}(\text{SiO}_3)_2 + \text{CO}_2 \rightarrow \frac{1}{2} \text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2$

5 e) Full decomposition (“the Diopside-MgO process”):



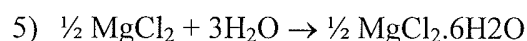
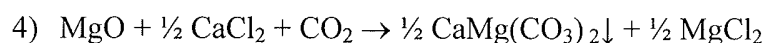
Thermal decomposition.



First rock melting reaction.

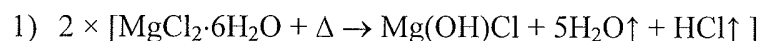


Second rock melting reaction. The MgCl_2 returns to #1.



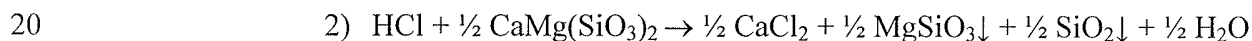
Regenerate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, return to #1.

15 f) Partial decomposition (“the Diopside-Mg(OH)Cl process”):

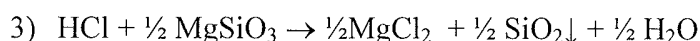


Thermal decomposition.

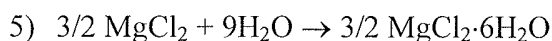
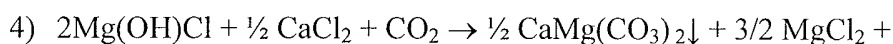
Twice as much $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is needed to trap the same amount of CO_2 .



First rock melting reaction.



Second rock melting reaction. Here the MgCl_2 returns to #1.



Regenerate $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, return to #1

Table 9. Summary of Processes

Example	Process	Flue gas source	Temp. °C ¹	% CO ₂ of flue gas ²	Detailed mass and energy balance of each process stream
10	CaSiO ₃ -Mg(OH)Cl	Coal	320-550	7.2% - 18%	Table 14
11	CaSiO ₃ -Mg(OH)Cl	Nat. gas	600	7.2% - 18%	Table 14
12	CaSiO ₃ -MgO	Coal	550	7.2% - 18%	Table 15
13	CaSiO ₃ -MgO	Nat. gas	600	7.2% - 18%	Table 15
14	MgSiO ₃ -Mg(OH)Cl	Coal	320-550	7.2% - 18%	Table 16
15	MgSiO ₃ -Mg(OH)Cl	Nat. gas	600	7.2% - 18%	Table 16
16	MgSiO ₃ -MgO	Coal	550	7.2% - 18%	Table 17
17	MgSiO ₃ -MgO	Nat. gas	600	7.2% - 18%	Table 17
18	Diopside-Mg(OH)Cl	Coal	320-550	7.2% - 18%	Table 18
19	Diopside-Mg(OH)Cl	Nat. gas	600	7.2% - 18%	Table 18
20	Diopside-MgO	Coal	550	7.2% - 18%	Table 19
21	Diopside-MgO	Nat. gas	600	7.2% - 18%	Table 19

1 – The temperature range of 320-550 °C includes models run at 320, 360, 400, 440 and 550 °C respectively.

2 – The CO₂ percentage of flue gas 7.2% - 18% includes models run at 7.2%, 10%, 14% and 18% respectively.

Calcium Silicate process:

The $\text{CaSiO}_3\text{-MgO}$ and $\text{CaSiO}_3\text{-Mg(OH)Cl}$ decomposition processes are further divided into two stages, the first step consists of a dehydration reaction where $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ is converted to $\text{MgCl}_2\cdot 2\text{H}_2\text{O} + 4 \text{H}_2\text{O}$ and the second step in which the $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ is converted to $\text{Mg(OH)Cl} + \text{HCl} + \text{H}_2\text{O}$ if partial decomposition is desired or required and $\text{MgO} + 2\text{HCl} + \text{H}_2\text{O}$ if total decomposition is desired or required. FIG. 15 describes a layout of this process.

Magnesium Silicate process:

The $\text{MgSiO}_3\text{-MgO}$ and $\text{MgSiO}_3\text{-Mg(OH)Cl}$ processes consists of a one chamber decomposition step in which the HCl from the decomposition chamber reacts with MgSiO_3 in the rock-melting reactor and the ensuing heat of reaction leaves the MgCl_2 in the dihydrate form $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ as it leaves the rock-melting chamber in approach to the decomposition reactor where it is converted to either MgO or Mg(OH)Cl as described earlier. This process may be preferred if calcium silicates are unavailable. The HCl emitted from the decomposition reacts with MgSiO_3 to form more MgCl_2 . The magnesium silicate process follows a different path from the calcium. The process starts from the “rock melting reaction $\text{HCl} + \text{silicate}$ ”, and then moves to the “decomposition reaction ($\text{MgCl}_2 + \text{heat}$)”, and lastly the absorption column. In the calcium silicate process, all the magnesium compounds rotate between the decomposition reaction and the absorption reaction. FIG. 16 describes the layout of this process.

Mixed Magnesium and Calcium Silicate “Diopside” process:

The intermediate process Diopside- MgO and Diopside- Mg(OH)Cl also involve a two stage decomposition consisting of the dehydration reaction $\text{MgCl}_2\cdot 6\text{H}_2\text{O} + \Delta \rightarrow \text{MgCl}_2\cdot 2\text{H}_2\text{O} + 4 \text{H}_2\text{O}$ followed by the decomposition reaction $\text{MgCl}_2\cdot 2\text{H}_2\text{O} + \Delta \rightarrow \text{MgO} + 2\text{HCl} + \text{H}_2\text{O}$ (full decomposition) or $\text{MgCl}_2\cdot 2\text{H}_2\text{O} + \Delta \rightarrow \text{Mg(OH)Cl} + \text{HCl} + \text{H}_2\text{O}$ partial decomposition. FIG. 17 describes a layout of this process.

The ensuing HCl from the decomposition then reacts with the Diopside $\text{CaMg(SiO}_3)_2$ in a two step “rock melting reaction.” The first reaction creates CaCl_2 through the reaction $2\text{HCl} + \text{CaMg(SiO}_3)_2 \rightarrow \text{CaCl}_2(aq) + \text{MgSiO}_3\downarrow + \text{SiO}_2\downarrow + \text{H}_2\text{O}$. The solids from the previous reaction are then reacted with HCl a second time to produce MgCl_2 through the reaction $\text{MgSiO}_3 + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{SiO}_2\downarrow + \text{H}_2\text{O}$. The CaCl_2 from the first rock melter is transported to the absorption column and the MgCl_2 from the second rock melter is transported to the decomposition reactor to make Mg(OH)Cl or MgO .

Basis of the reaction:

All of these examples assume 50% CO₂ absorption of a reference flue gas from a known coal fired plant of interest. This was done to enable a comparison between each example. The emission flow rate of flue gas from this plant is 136,903,680 tons per year and the CO₂ content of this gas is 10% by weight. This amount of CO₂ is the basis for examples 10 through 21 which is:

Amount of CO₂ present in the flue gas per year:

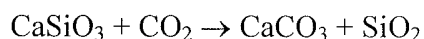
$$136,903,680 \text{ tons per year} * 10\% = 13,690,368 \text{ tons per year}$$

Amount of CO₂ absorbed per year.

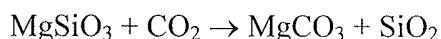
$$13,690,368 \text{ tons per year} * 50\% = 6,845,184 \text{ tons per year of CO}_2.$$

Since the amount of CO₂ absorbed is a constant, the consumption of reactants and generation of products is also a constant depending on the reaction stoichiometry and molecular weight for each compound.

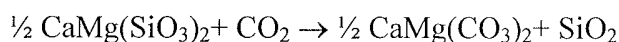
For all the examples of both the CaSiO₃-MgO and the CaSiO₃-Mg(OH)Cl process (examples 10-13) the overall reaction is:



For all the examples of both the MgSiO₃-MgO and the MgSiO₃-Mg(OH)Cl process (examples 14-17) the overall reaction is:



For all the examples of both the Diopside-MgO and the Diopside-Mg(OH)Cl process (examples 18-21) the overall reaction is:



The Aspen model enters the required inputs for the process and calculates the required flue gas to provide the heat needed for the decomposition reaction to produce the carbon dioxide absorbing compounds MgO, Mg(OH)₂ or Mg(OH)Cl. This flue gas may be from a natural gas or a coal plant and in the case of coal was tested at a range of temperatures from 320 °C to 550 °C. This flue gas should not be confused with the reference flue gas which was used a standard to provide a specific amount of CO₂ removal for each example. A process with a higher temperature flue gas would typically require a lesser amount of flue gas to capture the same amount of carbon dioxide from the basis. Also a flue gas with a greater carbon dioxide concentration would typically result in greater amount of flue gas needed to capture the carbon dioxide because there is a greater amount of carbon dioxide that needs to be captured.

The consumption of reactants and generation of products can be determined from the basis of CO₂ captured and the molecular weights of each input and each output for each example.

Table 10. Molecular Masses of Inputs and Outputs (all embodiments).

Compound	Molecular Weight
CaSiO ₃	116.16
MgSiO ₃	99.69
Diopside*	215.85
CaCO ₃	100.09
MgCO ₃	84.31
Dolomite*	184.40
SiO ₂	60.08
CO ₂	44.01

- 5 * Number of moles must be divided by 2 to measure comparable CO₂ absorption with the other processes,

For Examples 10-13:

The CaSiO₃ consumption is:

$$6,845,184 \text{ tons per year} * (116.16 / 44.01) = 18,066,577 \text{ tons per year.}$$

- 10 The CaCO₃ production is:

$$6,845,184 \text{ tons per year} * (100.09 / 44.01) = 15,559,282 \text{ tons per year.}$$

The SiO₂ production is:

$$6,845,184 \text{ tons per year} * (60.08 / 44.01) = 9,344,884 \text{ tons per year}$$

- 15 The same type of calculations may be done for the remaining examples. This following table contains the inputs and outputs for examples 10 through 21. Basis: 6,845,184 tons CO₂ absorbed per year.

Table 11. Mass Flows of Inputs and Outputs for Examples 10-21.

All measurements are in tons per year (TPY)			
	Examples		
	10-13	14-17	18-21
CO ₂ absorbed	6,845,184	6,845,184	6,845,184

All measurements are in tons per year (TPY)			
	Examples		
	10-13	14-17	18-21
INPUTS			
Flue Gas for CO ₂ Capture	136,903,680	136,903,680	136,903,680
10% CO ₂	13,690,368	13,690,368	13,690,368
CaSiO ₃	18,066,577		
MgSiO ₃		15,613,410	
Diopside			16,839,993
OUTPUTS			
SiO ₂	9,344,884	9,344,884	9,344,884
CaCO ₃	15,559,282		
MgCO ₃		13,111,817	
Dolomite			14,319,845

Running the Aspen models generated the following results for the heat duty for each step of the decomposition reaction, dehydration and decomposition. The results for each example are summarized in the table below.

Table 12. Power (Rate of Energy for each process at the particular basis of CO₂ absorption).

<u>HEAT BALANCE</u>							
<u>Process</u>		CaSiO ₃ -Mg(OH)Cl	CaSiO ₃ -MgO	MgSiO ₃ -Mg(OH)Cl	MgSiO ₃ -MgO	Diop.-Mg(OH)Cl	Diop.-MgO
<u>Examples</u>							
Dehydration Chamber (MW)		10,11	12,13	14,15	16,17	18,19	20,21
HEX TO DI(210 °C)		2670	1087	n/a	n/a	2614	1306
Source		HCl reacting with silicate					
Decomposition Chamber(MW)		1033	1297	1226	1264	1231	1374
Decomposition Temp. °C		210	450	210	450	210	450
Source		Flue Gas					
Total heat used for D&D* (MW)		3703	2384	1226	1264	3854	2680

*D&D equals dehydration and decomposition

Table 13. Percentage CO₂ captured as a function of flue gas temperature and CO₂ concentration. Examples 10 through 13.

Process	CaSiO ₃ -Mg(OH)Cl						CaSiO ₃ - MgO	CaSiO ₃ - Mg(OH)Cl	CaSiO ₃ - MgO
	Coal 320 °C	Coal 360 °C	Coal 400 °C	Coal 440 °C	Coal 550 °C		Coal 550 °C	Nat. gas 600 °C	Nat. gas 600 °C
Example #	10	10	10	10	10		12	11	13
% CO ₂									
7%	33%	45%	57%	70%	105%		83%	121%	96%
10%	24%	32%	41%	50%	75%		60%	87%	69%
14%	17%	23%	29%	36%	54%		43%	62%	50%
18%	13%	18%	23%	28%	42%		33%	48%	39%

A value of over 100% means that excess heat is available to produce more Mg(OH)Cl or MgO. FIG. 24 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition for examples 10 through 13 of the CaSiO₃-Mg(OH)Cl and CaSiO₃-MgO processes.

Table 14. Percentage CO₂ captured as a function of flue gas temperature and CO₂ concentration. Examples 14 through 17.

Process	MgSiO ₃ -Mg(OH)Cl					MgSiO ₃ - MgO	MgSiO ₃ - Mg(OH)Cl	MgSiO ₃ - MgO
	Coal 320 °C	Coal 360 °C	Coal 400 °C	Coal 440 °C	Coal 550 °C			
Flue Gas Source/Temp.								
Example #	14	14	14	14	14	16	15	17
% CO ₂								
7%	24%	34%	45%	55%	84%	86%	93%	96%
10%	17%	25%	32%	40%	61%	62%	67%	69%
14%	12%	18%	23%	28%	43%	44%	48%	49%
18%	10%	14%	18%	22%	34%	34%	37%	38%

FIG. 25 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition for examples 14 through 17 of the MgSiO₃-Mg(OH)Cl and MgSiO₃-MgO processes.

Table 15. Percentage CO₂ captured as a function of flue gas temperature and CO₂ concentration. Examples 18 through 21.

Process	Diopside-Mg(OH)Cl						Diop - MgO	Diop - Mg(OH)Cl	Diop - MgO
	Coal 320 °C	Coal 360 °C	Coal 400 °C	Coal 440 °C	Coal 550 °C		Coal 550 °C	Ngas 600 °C	Ngas 600 °C
Flue Gas Source/Temp.									
Example #	18	18	18	18	18		20	19	21
% CO ₂									
7%	28%	38%	48%	59%	88%		79%	101%	91%
10%	20%	27%	35%	42%	63%		57%	73%	65%
14%	14%	19%	25%	30%	45%		40%	52%	47%
18%	11%	15%	19%	23%	35%		31%	41%	36%

* Note Diop equals Diopside

FIG. 26 illustrates the percent CO₂ captured for varying CO₂ flue gas concentrations, varying temperatures, whether the flue gas was originated from coal or natural gas, and also whether the process relied on full or partial decomposition for examples 18 through 21 of the Diopside - Mg(OH)Cl and Diopside - MgO processes.

Table 16a. Mass and Energy Accounting for Examples 10 and 11 Simulation.

Process Stream Names →	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	FLUEGAS	H ₂ O	HCl	HCl Vapor
PH										
Temperature °C	112.6	95	149.9	150	95	25	100	25	200	250
Pressure psia	14.696	15	100	14.696	14.7	14.696	15.78	14.7	14.696	14.696
Mass VFrac	0	0.793	0	0	0	0	1	0	1	1
Mass SFrac	1	0.207	0	0.163	1	1	0	0	0	0
Mass Flow tonne/year	5.73E+07	3.96E+07	4.36E+07	5.21E+07	1.41E+07	164E+07	6.21E+07	1.80E+07	3.57E+07	3.57E+07
Volume Flow gal/min	11216.8	2.2E+07	17031.4	18643.542	2616.633	2126.004	3.11E+07	502184.16	3.30E+07	3.65E+07
Enthalpy MW	-22099.5	-3288.21	-17541.7	-21585.353	-5368.73	-7309.817	-2926.806	-9056.765	-11331.898	-11240.08
Density lb/cuft	160.371	0.059	80.305	87.619	169.173	241.725	0.063	1.125	0.034	0.031
H ₂ O	0	1.80E+07	2.79E+07	2.79E+07	0	0	3.10E+06	1.80E+07	2.54E+07	2.54E+07
HCl	0	0	0.004	0.004	0	0	0	0	1.03E+07	1.03E+07
CO ₂	0	0	0	0	0	0	6.21E+06	0	0	0
O ₂	0	0	0	0	0	0	6.21E+06	0	0	0
N ₂	0	0	0	0	0	0	4.65E+07	0	0	0
CaCO ₃	0	0	0	0	1.41E+07	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	5.73E+07	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	8.22E+06	0	0	0	0	0	0	0	0

Process Stream Names →	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	FLUEGAS	H ₂ O	HCl	HCl Vapor
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	3.43E+06	0	0	0	0	0	0	0	0
Ca ²⁺	0	0	5.65E+06	5.65E+06	0	0	0	0	0	0
Cl ⁻	0	1.00E+07	1.00E+07	1.00E+07	0	0	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	.007	0	1.64E+07	0	0	0	0
SiO ₂	0	0	0	8.47E+06	0	0	0	0	0	0

Table 16b. Mass and Energy Accounting for Examples 10 and 11 Simulation.

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
PH			9.453			9.453		
Temperature C	215	80	95	95	149.9	95	250	115
Pressure psia	14.696	14.696	14.7	14.7	100	14.7	14.696	14.696
Mass VFrac	.502	0	0	1	0	0	0	.165
Mass SFrac	.498	1	0	0	1	.152	1	.207
Mass Flow tonne/year	5.73E+07	5.73E+07	7.84E+07	5.27E+07	8.47E+06	9.26E+07	2.16E+07	3.96E+07
Volume Flow gal/min	3.03E+07	11216.796	33789.492	282E+07	1607.826	32401.78	3828.933	6.33E+06

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
Enthalpy MW	-1877.989	-22191.287	-32705.27	120.09	0	-38074.2	-7057.97	-4070.06
Density lb/cuft	.059	160.371	72.846	0.059	165.327	89.628	177.393	0.197
H ₂ O	2.54E+07	0	5.16E+07	0	0	5.16E+07	0	1.80E+07
HCl	3.40E+06	0	0	0	0	0	0	0
CO ₂	0	0	0.074	25.781	0	0.074	0	0
O ₂	0	0	2510.379	6.20E+06	0	2510.379	0	0
N ₂	0	0	8109.244	4.65E+07	0	8109.245	0	0
CaCO ₃	0	0	0	0	0	1.41E+07	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	2.14E+07	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	5.73E+07	0	0	0	0	0	0
Mg(OH)Cl	7.15E+06	0	0	0	0	0	2.16E+07	0
Mg(OH) ₂	0	0	0	0	0	0	0	8.22E+06
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	3324.433	0	0	3324.433	0	0
SO ₂	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	6.85E+06	0	0	6.85E+06	0	3.43E+06
Ca ²⁺	0	0	1644.031	0	0	1644.031	0	0
Cl ⁻	0	0	2.00E+07	0	0	2.00E+07	0	1.00E+07
CO ₃	0	0	61.424	0	0	61.424	0	0

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
-CO ₃	0	0	27.297	0	0	27.297	0	0
OH ⁻	0	0	690.278	0	0	690.278	0	0
CaSiO ₃	0	0	0	0	0.007	0	0	0
SiO ₂	0	0	0	0	8.47E+06	0	0	0

Table 17a. Mass and Energy Accounting for Examples 12 and 13 Simulation.

Process Stream Names →	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	FLUEGAS	H ₂ O	HCl	HCl Vapor
PH										
Temperature °C	271	255.5	149.8	150	95	25	100	25	200	450
Pressure psia	14.696	15	100	14.696	14.7	14.696	15.78	14.7	14.696	14.696
Mass VFrac	0	0	0	0	0	0	1	0	1	1
Mass SFrac	1	1	0	0.215	1	1	0	0	0	0
Mass Flow tonne/year	2.87E+07	2.37E+07	3.09E+07	3.94E+07	1.41E+07	1.64E+07	6.21E+07	1.80E+07	2.30E+07	2.30E+07
Volume Flow gal/min	5608.398	10220.835	10147.12	11758.176	2616.827	2126.004	3.11E+07	502184.16	1.93E+07	2.94E+07
Enthalpy MW	-10826.6	-11660.74	-11347.9	-15391.633	-5369.12	-7309.817	-2926.806	-9056.765	-6056.076	-5786.994
Density lb/cuft	160.371	72.704	95.515	105.035	169.173	241.725	0.063	1.125	0.037	0.024
H ₂ O	0	1.55E+07	1.52E+07	1.52E+07	0	0	3.10E+06	1.80E+07	1.27E+07	1.27E+07
HCl	0	0	0.015	0.015	0	0	0	0	1.03E+07	1.03E+07
CO ₂	0	0	0	0	0	0	6.21E+06	0	0	0
O ₂	0	0	0	0	0	0	6.21E+06	0	0	0
N ₂	0	0	0	0	0	0	4.65E+07	0	0	0
CaCO ₃	0	0	0	0	1.41E+07	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0

Process Stream Names →	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	FLUEGAS	H ₂ O	HCl	HCl Vapor
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	2.87E+07	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	8.22E+06	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	0	0	0	0	0	0	0	0
Ca ²⁺	0	0	5.65E+06	5.65E+06	0	0	0	0	0	0
Cl ⁻	0	0	1.00E+07	1.00E+07	0	0	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0.023	1.64E+07	0	0	0	0	0
SiO ₂	0	0	0	8.47E+06	0	0	0	0	0	0

Table 17b. Mass and Energy Accounting for Examples 12 and 13 Simulation.

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
PH			9.304			9.304		

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
Temperature °C	215	80	95	95	149.8	95	450	115
Pressure psia	14.696	14.696	14.7	14.7	100	14.7	14.696	14.696
Mass VFrac	0.502	0	0	1	0	0	0	0
Mass SFrac	0.498	1	0	0	1	0.221	1	1
Mass Flow tonne/year	2.87E+07	2.87E+07	4.98E+07	5.27E+07	8.47E+06	6.39E+07	5.68E+06	2.37E+07
Volume Flow gal/min	1.51E+07	5608.398	25330.305	2.82E+07	1607.826	22988.79	797.11	10220.84
Enthalpy MW	-9388.949	-11095.644	-21589.89	120.08	0	-26959.3	-2603.98	-11955.9
Density lb/cuft	0.059	160.371	61.662	0.059	165.327	87.199	223.695	72.704
H ₂ O	127E+07	0	3.63E+07	0	0	3.63E+07	0	1.55E+07
HCl	1.70E+07	0	0	0	0	0	0	0
CO ₂	0	0	0.145	79.255	0	0.145	0	0
O ₂	0	0	1919.222	6.20E+06	0	1919.222	0	0
N ₂	0	0	6199.3	4.65E+07	0	6199.301	0	0
CaCO ₃	0	0	0	0	0	1.41E+07	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *2W	1.07E+07	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	2.87E+07	0	0	0	0	0	0
Mg(OH)Cl	3.58E+06	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	8.22E+06
MgO	0	0	0	0	0	0	5.68E+06	0
MgHCO ₃ ⁺	0	0	2208.676	0	0	2208.676	0	0
SO ₂	0	0	0	0	0	0	0	0

Process Stream Names →	MgCl ₂ -2W	MgCl ₂ -6W	RECYCLE1	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
NO ₂	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	3.43E+06	0	0	3.43E+06	0	0
Ca ²⁺	0	0	1225.309	0	0	1225.309	0	0
Cl ⁻	0	0	1.00E+07	0	0	1.00E+07	0	0
CO ₃ ²⁻	0	0	110.963	0	0	110.963	0	0
HCO ₃ ⁻	0	0	63.12	0	0	63.12	0	0
OH ⁻	0	0	519.231	0	0	519.231	0	0
CaSiO ₃	0	0	0	0	0.023	0	0	0
SiO ₂	0	0	0	0	8.47E+06	0	0	0

Table 18a. Mass and Energy Accounting for Examples 14 and 15 Simulation.

Process Stream Names →	FLUEGAS	H ₂ O	H ₂ O	HCl Vapor	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
PH							
Temperature °C	100	25	26	250	200.7	200	200
Pressure psia	15.78	1	14.696	14.696	15	14.696	14.696
Mass VFrac	1	0	0.798	1	0.238	0	0.169
Mass SFrac	0	0	0.186	0	0	1	0.289
Mass Flow tons/year	1.37E+08	1.00E+07	1.58E+08	1.69E+07	2.31E+07	4.08E+07	3.26E+07
Volume Flow gal/min	62.21E+07	4569.619	4.91E+07	1.22E+07	5.22E+06	3828.933	5.33E+06
Enthalpy MW	-5853.92	-4563.814	-13984.7	-2861.732	0	-11194.13	-10932.15
Density lb/cuft	0.063	62.249	0.091	0.04	0.126	303.28	0.174
H ₂ O	6.85E+06	1.00E+07	5.19E+06	5.60E+06	8.37E+06	0	8.37E+06
HCl	0	0	0	1.13E+07	126399.9	0	126399.87

Process Stream Names →	FLUEGAS	H ₂ O	H ₂ O	HCl Vapor	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
CO ₂	1.37E+07	0	6.85E+06	0	0	0	0
C ₂	1.37E+07	0	1.37E+07	0	0	0	0
N ₂	1.03E+08	0	1.03E+08	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	4.08E+07	0
MgCl ₂ *4W	0	0	1.09E+07	0	0	0	0
MgCl ₂ *6W	0	0	1.83E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0.001	0	0	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
Mg ²⁺	0	0	0	0	3.74E+06	0	3.74E+06
Cl ⁻	0	0	0	0	1.09E+07	0	1.09E+07
CO ₃ ²⁻	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0
SiO ₂	0	0	0	0	0	0	9.24E+06
MgSiO ₃	0	0	0	0	0	0	174011.19

Table 18b. Mass and Energy Accounting for Examples 14 and 15 Simulation.

Process Stream Names →	MgCO ₃	MgSiO ₃	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
PH					.0864		6.24
Temperature °C	26	25		200.7	60	250	95
Pressure psia	14.696	14.696		15	44.088	14.696	44.088
Mass VFrac	0	0		0	0	0	0
Mass SFrac	1	1		1	0.248	1	0.268
Mass Flow tons/year	1.31E+07	1.56E+07	0	9.41E+06	1.71E+08	2.39E+07	3.39E+07
Volume Flow gal/min	1985.546	2126.004		1613.601	178707.499	3828.933	8016.874
Enthalpy MW	0	-6925.208	0	0	-18961.843	-7057.974	-12123.17
Density lb/cuft	187.864	208.902		165.967	27.184	177.393	120.206
H ₂ O	0	0		0	5.19E+06	0	1.00E+07
HCl	0	0		0	0	0	0
CO ₂	0	0		0	6.85E+06	0	0
O ₂	0	0		0	1.37E+07	0	0
N ₂	0	0		0	1.03E+08	0	0
MgCO ₃	1.31E+07	0		0	1.31E+07	0	0
MgCl ₂	0	0		0	0	0	0
MgCl ₂ *W	0	0		0	0	0	0
MgCl ₂ *2W	0	0		0	0	0	0
MgCl ₂ *4W	0	0		0	1.09E+07	0	0
MgCl ₂ *6W	0	0		0	1.83E+07	0	0
Mg(OH)Cl	0	0		0	0	2.39E+07	0
Mg(OH) ₂	0	0		0	0	0	9.07E+06

Process Stream Names →	MgCO ₃	MgSiO ₃	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
MgO	0	0		0	0	0	0
MgHCO ₃ ⁺	0	0		0	0.001	0	0
SO ₂	0	0		0	0	0	0
NO ₂	0	0		0	0	0	0
NO	0	0		0	0	0	0
Mg ²⁺	0	0		0	0	0	3.78E+06
Cl ⁻	0	0		0	0	0	1.10E+07
CO ₃ ²⁻	0	0		0	0	0	0
HCO ₃ ⁻	0	0		0	0	0	0
OH ⁻	0	0		0	0	0	0.029
SiO ₂	0	0		9.24E+06	0	0	0
MgSiO ₃	0	1.56E+07		174011.19	0	0	0

Table 19a. Mass and Energy Accounting for Examples 16 and 17 Simulation.

Process Stream Names →	FLUEGAS	H ₂ O	H ₂ O	HCl Vapor	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
PH			6.583				
Temperature °C	100	25	59.6	450	200	200	200
Pressure psia	15.78	1	14.696	14.696	15	14.696	14.696
Mass V/Frac	1	0	0.004	1	0	0	0
Mass S/Frac	0	0	0	0	1	1	1
Mass Flow tons/year	1.37E+08	1.00E+07	1.70E+07	1.41E+07	2.04E+07	2.04E+07	2.98E+07
Volume Flow gal/min	6.21E+07	4569.619	40446.86	1.26E+07	1914.466	1914.466	3522.292
Enthalpy MW	-5853.92	-4563.814	-7633.28	-1728.6	0	-5597.066	-9628.072
Density lb/cuft	0.063	62.249	11.94	0.032	303.28	303.28	240.308

Process Stream Names →	FLUEGAS	H ₂ O	H ₂ O	HCl Vapor	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
-H ₂ O	685.E+06	1.00E+07	1.68E+07	2.80E+06	0	0	0
-HCl	0	0	0	1.13E+07	0	0	0
CO ₂	1.37E+07	0	56280.04	0	0	0	0
O ₂	1.37E+07	0	18848.97	0	0	0	0
N ₂	1.03E+08	0	56346.51	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	2.04E+07	2.04E+07	2.04E+07
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	77.467	0	0	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
Mg ²⁺	0	0	744.857	0	0	0	0
Cl ⁻	0	0	0	0	0	0	0
CO ₃ ²⁻	0	0	1.19	0	0	0	0
HCO ₃ ⁻	0	0	3259.779	0	0	0	0
OH ⁻	0	0	0.109	0	0	0	0
SiO ₂	0	0	0	0	0	0	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0

Table 19b. Mass and Energy Accounting for Examples 16 and 17 Simulation.

Process Stream Names →	MgCO ₃	MgSiO ₃	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
PH					6.583		8.537
Temperature °C	59.6	25	60	200	60	450	95
Pressure psia	14.696	14.696	44.088	15	44.088	14.696	44.088
Mass VFrac	0	0	1	0	0	0	0
Mass SFrac	1	1	0	1	0.436	1	0.558
Mass Flow tons/year	1.31E+07	1.56E+07	1.23E+08	9.34E+06	3.01E+07	6.27E+06	1.63E+07
Volume Flow gal/min	1983.661	2126.004	1.76E+07	1607.826	9945.342	797.11	5155.55
Enthalpy MW	0	-6925.208	-1613.054	0	-12593.788	-2603.979	-7331.893
Density lb/cuft	187.864	208.902	0.199	165.327	86.031	223.695	89.76
H ₂ O	0	0	0	0	1.68E+07	0	7.20E+06
HCl	0	0	0	0	0	0	0
CO ₂	0	0	6.78E+06	0	56280.036	0	0
O ₂	0	0	1.37E+07	0	18848.966	0	0
N ₂	0	0	1.03E+08	0	56346.51	0	0
MgCO ₃	1.31E+07	0	0	0	1.31E+07	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	9.07E+06

Process Stream Names →	MgCO ₃	MgSiO ₃	RX2-VENT	SiO ₂	SLURRY	SOLIDS-1	SOLIDS-2
VgO	0	0	0	0	0	6.27E+06	0
VgHCO ₃ ⁺	0	0	343.415	0	77.467	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
Mg ²⁺	0	0	2722.849	0	744.857	0	14.282
Cl ⁻	0	0	0	0	0	0	0
CO ₃ ²⁻	0	0	4.344	0	1.19	0	0
HCO ₃ ⁻	0	0	14439.982	0	3259.779	0	0
OH ⁻	0	0	0.481	0	0.109	0	19.989
SiO ₂	0	0	0	9.34E+06	0	0	0
MgSiO ₃	0	1.56E+07	0	0	0	0	0

Table 20a. Mass and Energy Accounting for Examples 18 and 19 Simulation.

Process Stream Names →	5	CaCl ₂ -2W	FLUEGA S	H ₂ O	HCl	HCl- VENT	HCIVAP2	HCl Vapor	HCIVENT 2	MELT1	MELT2	MELT3
PH												
Temperature °C	200	160	100	25	250	100	349.1	349.1	160	160	160	100
Pressure psia	14.696	14.696	15.78	1	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
Mass VFrac	0.378	0.473	1	0	1	1	1	1	1	0.311	0	0
Mass SFrac	0.622	0	0	0	0	0	0	0	0	0.342	1	0.291
Mass Flow tons/year	6.32E+07	2.40E+07	1.37E+08	1.00E+0 7	3.94E+0 7	0.001	197E+07	1.97E+07	26.688	3.65E+07	1.25E+07	3.22E+07
Volume Flow gal/min	2.29E+07	1.02E+07	6.21E+07	4569.619	3.64E+0 7	0.001	1.82E+07	1.82E+07	11.834	1.02E+07	1866.916	9636.543

Process Stream Names →	5	CaCl ₂ -2W	FLUEGA S	H ₂ O	HCl	HCl- VENT	HCIVAP2	HCl Vapor	HCIVENT 2	MELT1	MELT2	MELT3
Enthalpy MW	-19530.7	-8042.026	-5853.92	4563.814	-11241.7	0	-5620.856	-5620.856	-0.002	-13498.19	-5456.154	12759.563
Density lb/cuft	0.079	0.067	0.063	62.249	0.031	0.075	0.031	0.031	0.064	0.102	190.163	94.933
H ₂ O	2.29E+07	1.54E+07	6.85E+06	1.00E+07	2.08E+07	0	1.40E+07	1.40E+07	0	1.54E+07	0	1.54E+07
HCl	983310.7	0	0	0	1.13E+07	0.001	5.67E+06	5.67E+06	26.688	26.688	0	0.001
CO ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
O ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
N ₂	0	0	1.03E+08	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	3.73E+07	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	2.07E+06	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	2494.617	0	0	0	0	0	0	0	2494.617	0	1.89E+06
Ca ²⁺	0	3.11E+06	0	0	0	0	0	0	0	3.11E+06	0	4128.267
Cl ⁻	0	5.51E+06	0	0	0	0	0	0	0	5.51E+06	0	5.51E+06

Process Stream Names →	5	CaCl ₂ -2W	FLUEGA S	H ₂ O	HCl	HCl- VENT	HCIVAP2	HCl Vapor	HCIVENT 2	MELT1	MELT2	MELT3
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	11965.65 9	11965.65 9	0
SiO ₂	0	0	0	0	0	0	0	0	0	4.67E+06	4.67E+06	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0	0	0	7.80E+06	7.80E+06	36.743
DIOPSIDE	0	0	0	0	0	0	0	0	0	0	0	0
DOLOMITE	0	0	0	0	0	0	0	0	0	0	0	0

Table 20b. Mass and Energy Accounting for Examples 18 and 19 Simulation.

Process Stream Names →	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	RECYCLE	RECYCLE	RECYCLE-	SiO ₂	SLURRY	SOLIDS	SOLIDS-1	SOLIDS- 2	VENT
PH								5.163			6.252	
Temperature °C	25	100	100	95	95	95	100	95	95	250	95	95
Pressure psia	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
Mass VFrac	0	0	0	0	0	0	0	0	0	0	0	1
Mass SFrac	1	0	1	0.828	0.828	1	1	0.317	1	1	0.268	0
Mass Flow tons/year	168E+07	2.28E+07	4.74E+07	5.73E+07	5.73E+07	1.58E+07	9.34E+06	1.95E+08	1.43E+07	2.39E+07	3.39E+07	1.23E+08
Volume Flow gal/min	1063.002	8028.716	8412.597	13075.55	13075.55	2804.199	1607.827	185622	2276.765	3828.933	8017.333	5.85E+07
Enthalpy MW	-7167.458	0	-16601.2	-21023.6	-21023.6	-5537.26	0	-27714.4	0	-7057.97	-12113.4	-1510.76
Density lb/cuft	450.627	80.836	160.371	124.605	124.605	160.371	165.327	29.855	178.921	177.393	120.2	0.06
H ₂ O	0	1.54E+07	0	9.84E+07	9.84E+07	0	0	9.84E+06	0	0	1.00E+07	0
HCl	0	0	0	0	0	0	0	0	0	0	0	0

Process Stream Names →	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	RECYCLE	RECYCLE-	SiO ₂	SLURRY	SOLIDS	SOLIDS-1	SOLIDS- 2	VENT
CO ₂	0	0	0	0	0	0	6.85E+06	0	0	0	6.85E+06
O ₂	0	0	0	0	0	0	1.37E+07	0	0	0	1.37E+07
N ₂	0	0	0	0	0	0	1.03E+08	0	0	0	1.03E+08
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	4.74E+07	4.74E+07	1.58E+07	0	4.74E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	2.39E+07	0	0
Mg(OH) ₂	0	0	0	12011.06	0	0	12011.06	0	0	9.07E+06	0
MgO	0	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	11.135	0	0	11.135	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	1.89E+06	0	0	0	0	0	0	0	3.78E+06	0
Ca ²⁺	0	4128.267	0	0	0	0	0	0	0	0	0
Cl ⁻	0	5.51E+06	0	4.627	0	0	4.627	0	0	1.10E+07	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0.03	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	0	0
SiO ₂	0	0	0	0	0	9.34E+06	0	0	0	0	0
MgSiO ₃	0	0	0	0	0	36.743	0	0	0	0	0

Process Stream Names →	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	RECYCLE	RECYCLE-	SiO ₂	SLURRY	SOLIDS	SOLIDS-1	SOLIDS-2	VENT
CIOPSIDE	1.68E+07	0	0	0	0	0	0	0	0	0	0
DOLOMITE	0	0	0	0	0	0	1.43E+07	1.43E+07	0	0	0

Table 21a. Mass and Energy Accounting for Examples 20 and 21 Simulation.

Process Stream Names →	5	CaCl ₂ -2W	FLUEGAS	H ₂ O	HCl	HCl-VENT	HCIVAP2	HCl Vapor	HCIVENT2	MELT1	MELT2	MELT3
PH												
Temperature °C	200	160	100	25	450	100	449.5	449.5	160	160	160	100
Pressure psia	14.696	14.696	15.78	1	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
Mass VFrac	0.378	0.256	1	0	1	1	1	1	1	0.148	0	0
Mass SFrac	0.622	0	0	0	0	0	0	0	0	0.423	1	0.371
Mass Flow tons/year	3.16E+07	1.70E+07	1.37E+08	1.00E+07	2.54E+07	0.006	1.27E+07	1.27E+07	10.275	2.95E+07	1.25E+07	2.52E+07
Volume Flow gal/min	1.14E+07	3.91E+06	6.21E+07	4569.619	2.94E+07	0.002	1.47E+07	1.47E+07	4.556	3.91E+06	1866.915	6342.437
Enthalpy MW	-9765.36	5388.055	-5853.92	4563.814	-5787.5	0	2893.751	2893.751	-0.0001	-10844.21	-5456.149	-9602.42
Density lb/cuft	0.079	0.124	0.063	62.249	0.025	0.075	0.025	0.025	0.064	0.215	190.163	112.823
H ₂ O	1.15E+07	8.41E+06	6.85E+06	1.00E+07	1.40E+07	0	7.00E+06	7.00E+06	0	8.41E+06	0	8.41E+06
HCl	491655.4	0	0	0	1.13E+07	0.006	5.67E+06	5.67E+06	10.275	10.275	0	0.006
CO ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
O ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
N ₂	0	0	1.03E+08	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0	0

Process Stream Names →	5	CaCl ₂ - 2W	FLUEGAS	H ₂ O	HCl	HCl- VENT	HCIVAP2	HCl Vapor	HCIVENT2	MELT1	MELT2	MELT3
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	1.86E+07	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	1.04E+06	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	2494.624	0	0	0	0	0	0	0	2494.624	0	1.89E+06
Ca ²⁺	0	3.11E+06	0	0	0	0	0	0	0	3.11E+06	0	4119.258
Cl ⁻	0	5.51E+06	0	0	0	0	0	0	0	5.51E+06	0	5.51E+06
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	11939.547	11939.547	0
SiO ₂	0	0	0	0	0	0	0	0	0	4.67E+06	4.67E+06	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0	0	0	7.80E+06	7.80E+06	14.153
DIOPSIDE	0	0	0	0	0	0	0	0	0	0	0	0
DOLOMITE	0	0	0	0	0	0	0	0	0	0	0	0

Table 21b. Mass and Energy Accounting for Examples 20 and 21 Simulation.

Process Stream Names →	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	RECYCLE	RECYCLE-	SiO ₂	SLURRY	SOLIDS	SOLIDS-1	SOLIDS- 2	VENT
PH				-0.879			5.271			8.545	
Temperature °C	25	100	100	95	95	100	95	95	450	95	95
Pressure psia	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
Mass VFrac	0	0	0	0	0	0	0	0	0	0	1
Mass SFrac	1	0	1	0	0.484	1	1	0.177	1	1	0.558
Mass Flow tons/year	1.68E+07	1.58E+07	1.58E+07	3.27E+07	1.58E+07	9.34E+06	1.70E+08	1.43E+07	6.27E+06	1.63E+07	1.23E+08
Volume Flow gal/min	1063.002	4734.61	2804.199	10786.59	2804.199	1607.826	183332.5	2276.772	797.11	5155.892	5.85E+07
Enthalpy MW	-7167.458	0	-5533.74	-13087	-5537.26	0	-19788.2	0	-2603.98	-7331.92	-1510.64
Density lb/cuft	450.627	94.994	160.371	86.167	160.371	165.327	26.409	178.921	223.695	89.754	0.06
H ₂ O	0	8.41E+06	0	1.68E+07	0	0	1.68E+07	0	0	7.20E+06	0
HCl	0	0	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	6.85E+06	0	0	0	6.85E+06
O ₂	0	0	0	0	0	0	1.37E+07	0	0	0	1.37E+07
N ₂	0	0	0	0	0	0	1.03E+08	0	0	0	1.03E+08
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	1.58E+07	1.58E+07	1.58E+07	0	1.58E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	11678.01	0	0	11678.01	0	0	9.07E+06	0
MgO	0	0	0	0	0	0	0	0	6.27E+06	0	0
MgHCO ₃ ⁺	0	0	0	908.901	0	0	908.901	0	0	0	0

Process Stream Names →	MgCaSiO3	MgCl ₂ --H	MgCl ₂ -H	RECYCLE	RECYCLE-	SiO ₂	SLURRY	SOLIDS	SOLIDS-1	SOLIDS- 2	VENT
SO ₂	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	1.89E+06	0	0	0	0	0	0	0	14.555	0
Ca ²⁺	0	4119.258	0	0	0	0	0	0	0	0	0
Cl ⁻	0	5.51E+06	0	377.667	0	0	377.667	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0.006	0	0	0.006	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	0	0
SiO ₂	0	0	0	0	0	9.34E+06	0	0	0	0	0
MgSiO ₃	0	0	0	0	0	14.153	0	0	0	0	0
DIOPSIDE	1.68E+07	0	0	0	0	0	0	0	0	0	0
DOLOMITE	0	0	0	0	0	0	1.43E+07	1.43E+07	0	0	0

Example 22: Decomposition of other salts.

The thermal decomposition of other salts has been measured in lab. A summary of some test results are shown in the table below.

Table 22. Decomposition of other salts.

Salt	Temp.°C	Time (min.)	Results
Mg(NO ₃) ₂	400	30	63% decomposition. Reaction is $\text{Mg(NO}_3)_2 \rightarrow \text{MgO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$
Mg(NO ₃) ₂	400	45	64% decomposition.
Mg(NO ₃) ₂	400	90	100% decomposition
Mg(NO ₃) ₂	400	135	100% decomposition
Ca(NO ₃) ₂	400	30	<25% decomposition Reaction is $\text{Ca(NO}_3)_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$
Ca(NO ₃) ₂	600	50	61% decomposition
Ca(NO ₃) ₂	600	Overnight	100% decomposition
LiCl	450	120	~0% decomposition

5 **Example 22: Two, Three and Four-Chamber Decomposition Models**

Table 23 (see below) is a comparison of the four configurations corresponding to FIGS. 31-34. Depicted are the number and description of the chambers, the heat consumed in MW (Megawatts), the percentage of heat from that particular source and the reduction of required external heat in kW-H/tonne of CO₂ because of available heat from other reactions in the process, namely the hydrochloric acid reaction with mineral silicates and the condensation of hydrochloric acid. In the FIG. 34 example, the hot flue gas from the open-cycle natural gas plant also qualifies.

10

Example 23: Output Mineral Compared with Input Minerals—Coal

In this case study involving flue gas from a coal-based power plant, Table 24 illustrates that the volume of mineral outputs (limestone and sand) are 83% of the volume of input minerals (coal and inosilicate). The results summarized in Table 24 are based on a 600 MWe coal plant; total 4.66 E6 tonne CO₂, includes CO₂ for process-required heat.

15

Example 24: Output Mineral Compared with Input Minerals—Natural Gas

5 In this case study summarized in Table 25 (below) involving flue gas from a natural gas-based power plant, the “rail-back volume” of minerals is 92% of the “rail-in volume” of minerals. The results summarized in Table 25 are (based on a 600 MWe CC natural gas plant; total 2.41 E6 tonne CO₂, which includes CO₂ for process-required heat.

Table 23. Two, Three and Four-Chamber Decomposition Results

Chamber Description						
Example	No. of Chambers	Pre-heat Cold Flue Gas	Pre Heat from Steam	Pre-Heat Mineral Dissolution Reactor		Decomposition
				Silicate Reaction	HCl Heat Recovery	
FIG. 31 Cold Flue Gas Pre Heat						
MW of Heat	3	83.9	Not used	286	563	86.8
Percentage of Total Heat		8.2%	Not used	28.0%	55.2%	8.5%
Reduction kW-Hr/tonne		-506.7	Not used	-1727.4	-3400.5	Not a reduction
FIG. 32 Cold Flue Gas and Steam Pre -Heat						
MW of Heat	4	83.9	8.7	286	563	82.2
Percentage of Total Heat		8.2%	0.8%	27.9%	55.0%	8.0%
Reduction kW-Hr/tonne		-506.7	-52.5	-1727.4	-3400.5	Not a reduction
FIG. 33 Nat Gas Only						
MW of Heat	2	Not used	Not used	279	586	129.3
Percentage of Total Heat		Not used	Not used	28%	59%	13%
Reduction kW-Hr/tonne		Not used	Not used	-1685.1	-3539.4	Not a reduction
FIG. 34 Hot Flue Gas Only						
MW of Heat	2	Not used	Not used	243	512	112.9
Percentage of Total Heat		Not used	Not used	28%	59%	13%
Reduction kW-Hr/tonne		Not used	Not used	-1467.7	-3092.4	-681.9

Table 24. Coal Scenario — Volume of Mineral Outputs Compared with Volume of Mineral Inputs

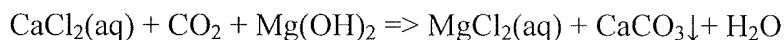
		Metric Units		English Units	
Parameter	Bulk Density (Tonne/m ³)	Mass (10 ⁶ Tonne/yr)	Volume (10 ⁶ m ³ /yr)	Mass (10 ⁶ Ton/yr)	Volume (10 ⁶ ft ³ /yr)
Coal	0.8	1.57	1.97	1.73	69.5
CaSiO ₃	0.71	12.30	17.32	13.56	611.8
Coal + CaSiO ₃					681.25
CaCO ₃	0.9	10.60	11.78	11.68	415.9
SiO ₂	1.5	6.35	4.23	7.00	149.5
CaCO ₃ + SiO ₂	n/a	16.95	16.01	18.68	565.4
RATIO OF MINERAL VOLUME OUT/MINERAL VOLUME IN =					83.00%

Table 25. Natural Gas Scenario — Volume of Mineral Outputs Compared with Volume of Mineral Inputs

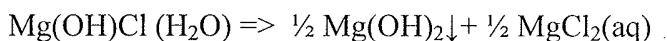
		Metric Units		English Units	
Parameter	Bulk Density (Tonne/m ³)	Mass (10 ⁶ Tonne/yr)	Volume (10 ⁶ m ³ /yr)	Mass (10 ⁶ Ton/yr)	Volume (10 ⁶ ft ³ /yr)
Coal	0.8	1.57	1.97	1.73	69.5
CaSiO ₃	0.71	12.30	17.32	13.56	611.8
Coal + CaSiO ₃					681.25
CaCO ₃	0.9	10.60	11.78	11.68	415.9
SiO ₂	1.5	6.35	4.23	7.00	149.5
CaCO ₃ + SiO ₂	n/a	16.95	16.01	18.68	565.4
RATIO OF MINERAL VOLUME OUT/MINERAL VOLUME IN =					83.00%

Example 25: Selective production of magnesium hydroxide by disproportionation of water and magnesium chloride

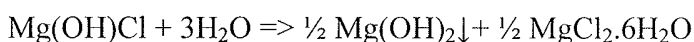
Mg(OH)₂ can be used in the following reaction to produce limestone from CO₂ gas.



5 In order to optimize production of Mg(OH)₂, upon conversion of MgCl₂ to Mg(OH)Cl, the amount of water in the reaction chamber will be adjusted to favor Mg(OH)₂ precipitation. Specifically, when Mg(OH)Cl and MgCl₂ is provided in a large enough volume of water, the magnesium hydroxide precipitates, as it is virtually insoluble, whereas the magnesium chloride forms an aqueous solution. Thus the two compounds may be efficiently separated. Note the water (H₂O) in the reaction below, does not become part of the products,
10 it merely solvates the Mg²⁺ and Cl⁻ so they become an ionic solution.



If the amount of water is reduced until the a ratio of about 6 to 1 relative to magnesium, it would be possible to form MgCl₂·6H₂O instead of MgCl₂(aq). The equation
15 would be as follows:



Thus, by maintaining a MgCl₂ to water ratio of greater than or equal to 6 to 1, production of aqueous MgCl₂ and solid Mg(OH)₂ is favored. Thus, an example set of CO₂ capture reactions can be represented as:

- 20 i) $\text{MgCl}_2 \cdot \text{H}_2\text{O} \Rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{H}_2\text{O} + \text{HCl}$
 ii) $\text{HCl} + \text{CaSiO}_3 \Rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{SiO}_2$
 iii) $\text{Mg}(\text{OH})\text{Cl} + \text{MgCl}_2 + \text{H}_2\text{O} \Rightarrow \text{Mg}(\text{OH})_2 + \text{MgCl}_2 + \text{H}_2\text{O}$
 iv) $\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 + \text{CO}_2 + \text{CaCl}_2 \Rightarrow \text{MgCl}_2 + \text{CaCO}_3 + \text{H}_2\text{O}$

With an overall reaction of: $\text{CaSiO}_3 \text{ CO}_2 \Rightarrow \text{CaCO}_3 + \text{SiO}_2$.

25 This system is shown in the the Aspen diagram of FIG. 38A-I and FIG. 39A-I. The outlined rectangle in the center of the diagram is around the defined “water disproportionator”. At the top of the rectangle, Mg(OH)Cl, stream SOLIDS-1, is leaving the decomposition reactor labeled “DECOMP”. Then in the module labeled MGOH2, the Mg(OH)Cl is mixed the aqueous MgCl₂ from the absorption column, stream RECYCLE2.
 30 They leave as a slurry from the unit as stream “4”, pass through a heat exchanger and send heat to the decomposition chamber. The stream is then named “13” which passes through a separation unit which separates the stream into stream MGCLSLRY (MgCl₂·6H₂O almost) and stream SOLIDS-2, which is the Mg(OH)₂ heading to the absorption column.

* * * * *

5 All of the methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of particular embodiments, it will be apparent to those of skill in the art that variations may be applied to the methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

REFERENCES

The following references, to the extent that they provide exemplary procedural or other details supplementary to those set forth herein, are specifically incorporated herein by reference.

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WHAT IS CLAIMED IS:

1. A method of sequestering carbon dioxide produced by a source, comprising:
 - (a) reacting MgCl_2 or a hydrate thereof with water in a first admixture under conditions suitable to form a first product mixture comprising a first step (a) product comprising Mg(OH)Cl and a second step (a) product comprising HCl ;
 - (b) reacting some or all of the Mg(OH)Cl from step (a) with a quantity of water and a quantity of MgCl_2 in a second admixture under conditions suitable to form a second product mixture comprising a first step (b) product comprising Mg(OH)_2 and a second step (b) product comprising MgCl_2 , wherein the quantity of water is sufficient to provide a molar ratio of water to MgCl_2 of greater than or equal to 6 to 1 in the second product mixture;
 - (c) admixing some or all of the Mg(OH)_2 from the first step (b) product with CaCl_2 or a hydrate thereof and carbon dioxide produced by the source in a third admixture under conditions suitable to form a third product mixture comprising a first step (c) product comprising MgCl_2 or a hydrate thereof, a second step (c) product comprising CaCO_3 , and a third step (c) product comprising water; and
 - (d) separating some or all of the CaCO_3 from the third product mixture, whereby some or all of the carbon dioxide is sequestered as CaCO_3 .
2. The method of claim 1, wherein some or all of the water in step (a) is present in the form of a hydrate of the MgCl_2 .
3. The method according to either claims 1 or 2, wherein the molar ratio of water to MgCl_2 in the second product mixture is between 6 and 10.
4. The method of claim 3, wherein the molar ratio of water to MgCl_2 in the second product mixture is between about 6 and about 7.
5. The method according to any one of claims 1-4, further comprising monitoring the concentration of Mg in the second admixture.
6. The method of claim 5, wherein the amount of Mg(OH)Cl or the quantity of water in a second admixture is adjusted based on said monitoring.

7. The method according to any one of claims 1-6, wherein the MgCl_2 of step (a) is a MgCl_2 hydrate.
8. The method of claim 7, wherein the MgCl_2 hydrate of step (a) is $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.
9. The method according to any one of claims 1-8, wherein the MgCl_2 of step (a) is greater than 90% by weight $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$.
10. The method according to any one of claims 1-9, wherein the first step (a) product comprises greater than 90% by weight $\text{Mg}(\text{OH})\text{Cl}$.
11. The method according to any one of claims 1-10, further comprising separating the step (b) products.
12. The method of claim 11, wherein the $\text{Mg}(\text{OH})_2$ product of step (b) is a solid and wherein separating the step (b) products comprises separating some or all of the solid $\text{Mg}(\text{OH})_2$ from the water and the MgCl_2 .
13. The method according to any one of claims 1-12, wherein the MgCl_2 product of step (b) is aqueous MgCl_2 .
14. The method according to any one of claims 1-13, wherein some or all of the MgCl_2 formed in step (b) or step (c) is the MgCl_2 used in step (a).
15. The method according to any one of claims 1-13, where some or all of the water in step (a) is present in the form of steam or supercritical water.
16. The method according to any one of claims 1-15, where some or all of the water of step (a) is obtained from the water of step (c).
17. The method of any one of claims 1-16, further comprising:
 - (e) admixing a calcium silicate mineral with HCl under conditions suitable to form a third product mixture comprising CaCl_2 , water, and silicon dioxide.
18. The method of claim 17, where some or all of the HCl in step (e) is obtained from step (a).
19. The method of claim 17, wherein step (e) further comprises agitating the calcium silicate mineral with HCl .

20. The method according to any one of claims 17-19, wherein some or all of the heat generated in step (e) is recovered.
21. The method according to any one of claims 17-20, where some or all of the CaCl_2 of step (c) is the CaCl_2 of step (e).
22. The method according to any one of claims 17-21, further comprising a separation step, wherein the silicon dioxide is removed from the CaCl_2 formed in step (e).
23. The method according to any one of claims 17-22, where some or all of the water of step (a) is obtained from the water of step (e).
24. The method according to any one of claims 17-22, wherein the calcium silicate mineral of step (e) comprises a calcium inosilicate.
25. The method according to any one of claims 17-22, wherein the calcium silicate mineral of step (e) comprises CaSiO_3 .
26. The method according to any one of claims 17-22, wherein the calcium silicate mineral of step (e) comprises diopside ($\text{CaMg}[\text{Si}_2\text{O}_6]$) or tremolite $\text{Ca}_2\text{Mg}_5\{[\text{OH}]\text{Si}_4\text{O}_{11}\}_2$.
27. The method according to any one of claims 17-22, wherein the calcium silicate further comprises iron and or manganese silicates.
28. The method of claim 27, wherein the iron silicate is fayalite ($\text{Fe}_2[\text{SiO}_4]$).
29. The method according to any one of claims 1-28, wherein the carbon dioxide is in the form of flue gas, wherein the flue gas further comprises N_2 and H_2O .
30. The method according to any one of claims 1-29, wherein suitable reacting conditions of step (a) comprise a temperature from about 200 °C to about 500 °C.
31. The method of claim 30, wherein the temperature is from about 230 °C to about 260 °C.
32. The method of claim 30, wherein the temperature is about 250 °C.
33. The method of claim 30, wherein the temperature is from about 200 °C to about 250 °C.

34. The method of claim 30, wherein the temperature is about 240 °C.
35. The method according to any one of claims 1-34, wherein the suitable reacting conditions of step (b) comprise a temperature from about 140 °C to about 240 °C.
36. The method according to any one of claims 1-35, wherein suitable reacting conditions of step (c) comprise a temperature from about 20 °C to about 100 °C.
37. The method of claim 36, wherein the temperature is from about 25 °C to about 95 °C.
38. The method according to any one of claims 17-37, wherein suitable reacting conditions of step (e) comprise a temperature from about 50 °C to about 200 °C.
39. The method of claim 38, wherein the temperature is from about 90 °C to about 150 °C.
40. The method according to any one of claims 1-39, wherein some or all of the hydrogen chloride of step (a) is admixed with water to form hydrochloric acid.
41. The method of claim 1, wherein step (a) occurs in one, two or three reactors.
42. The method of claim 1, wherein step (a) occurs in one reactor.

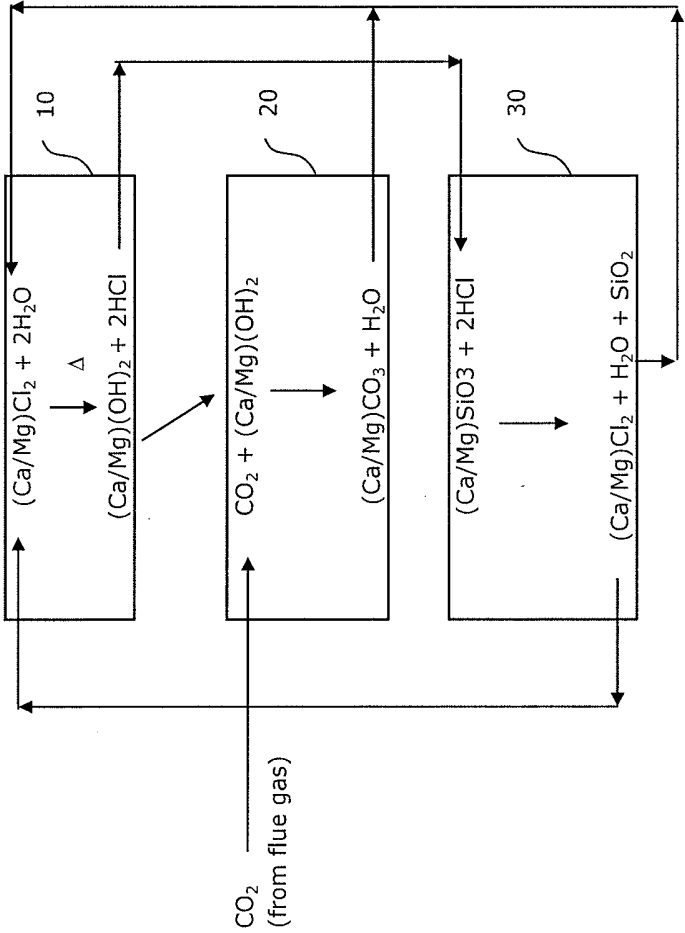


FIG. 1

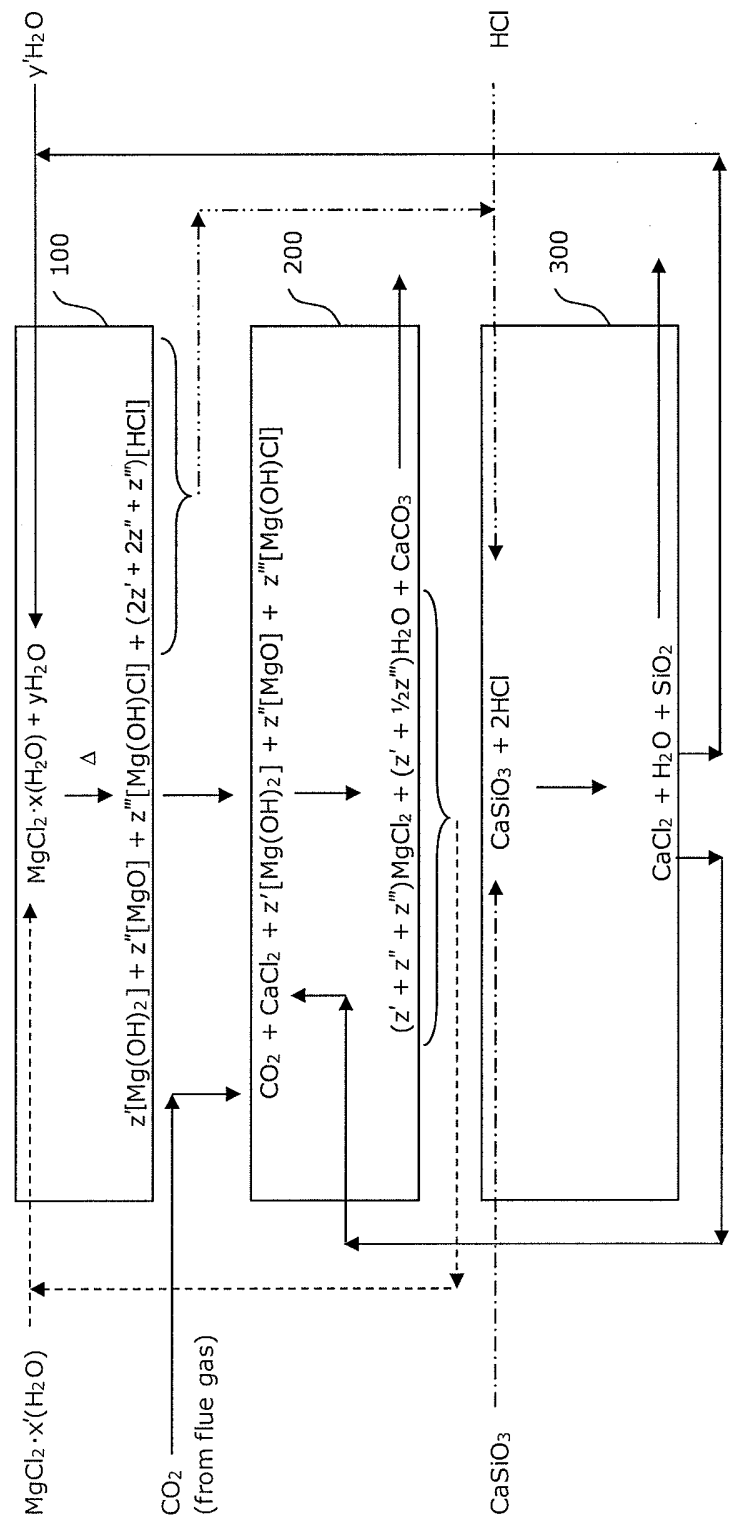


FIG. 2

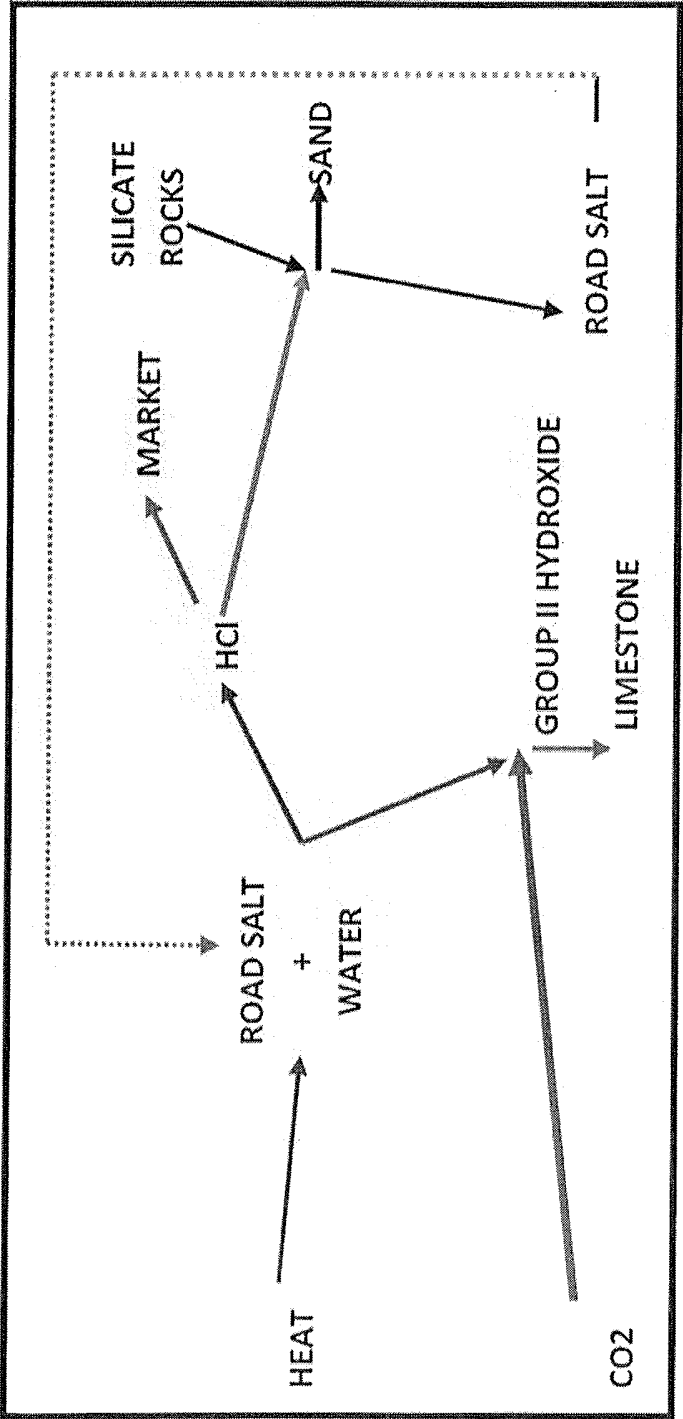


FIG. 3

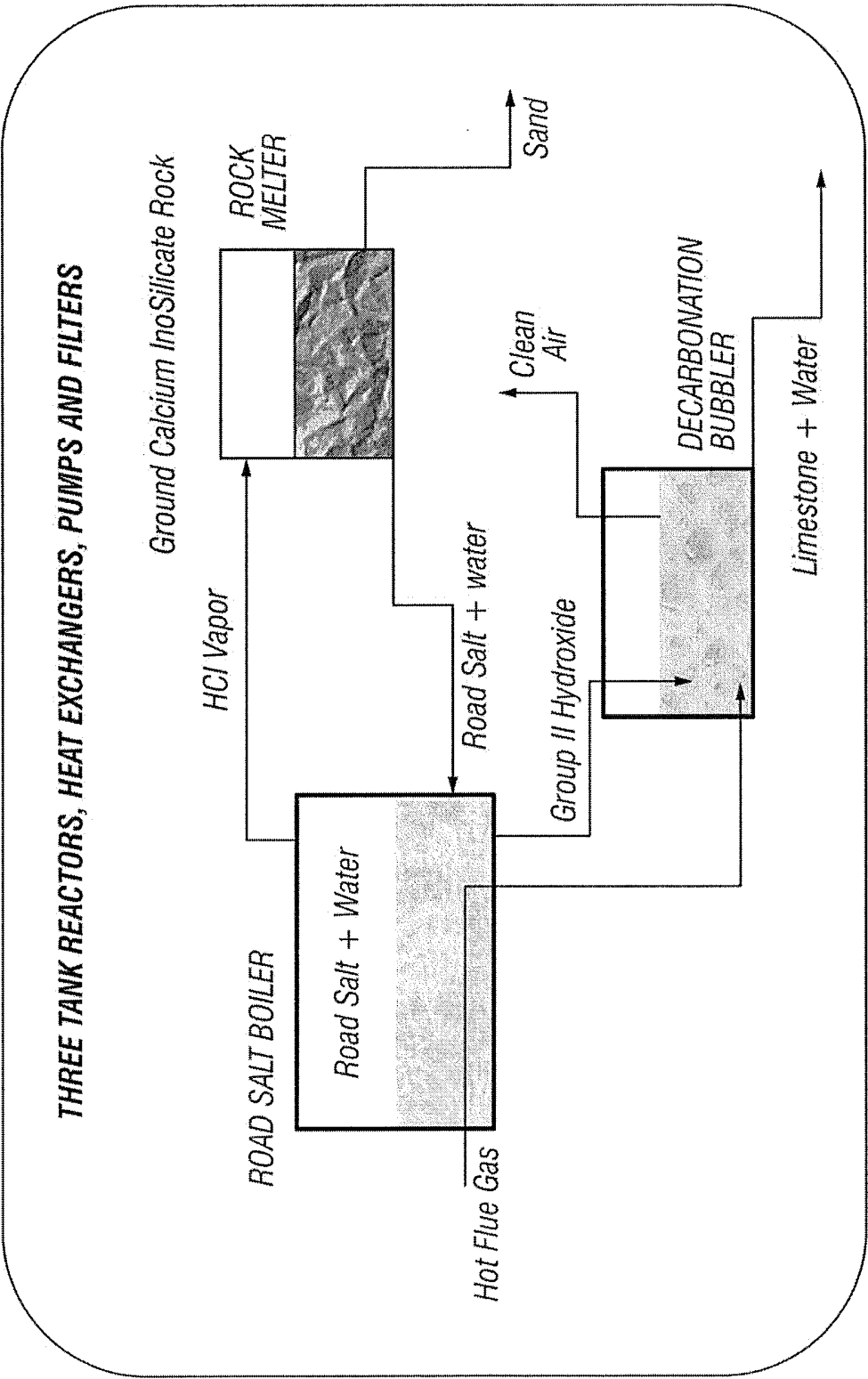


FIG. 4

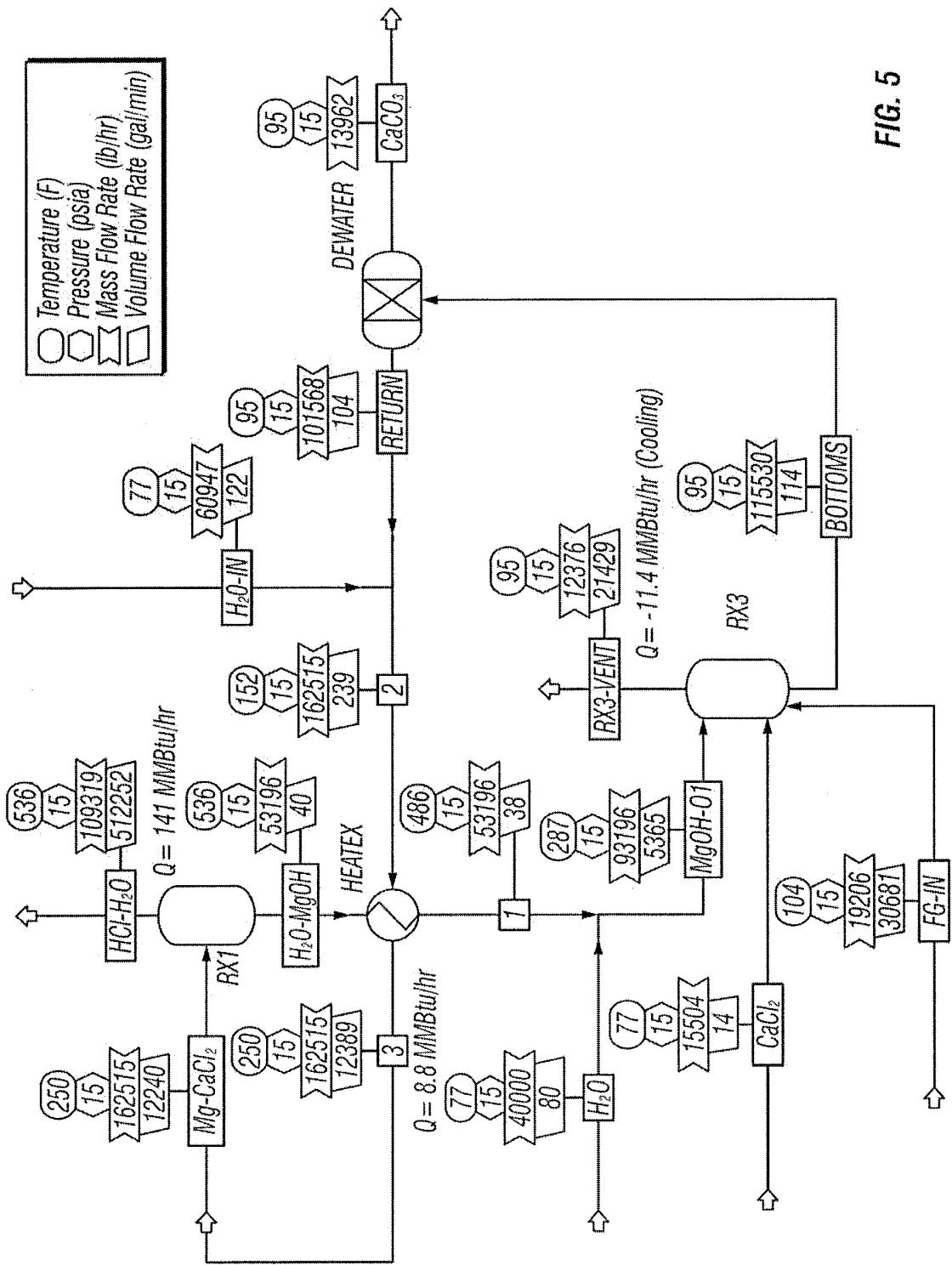


FIG. 5

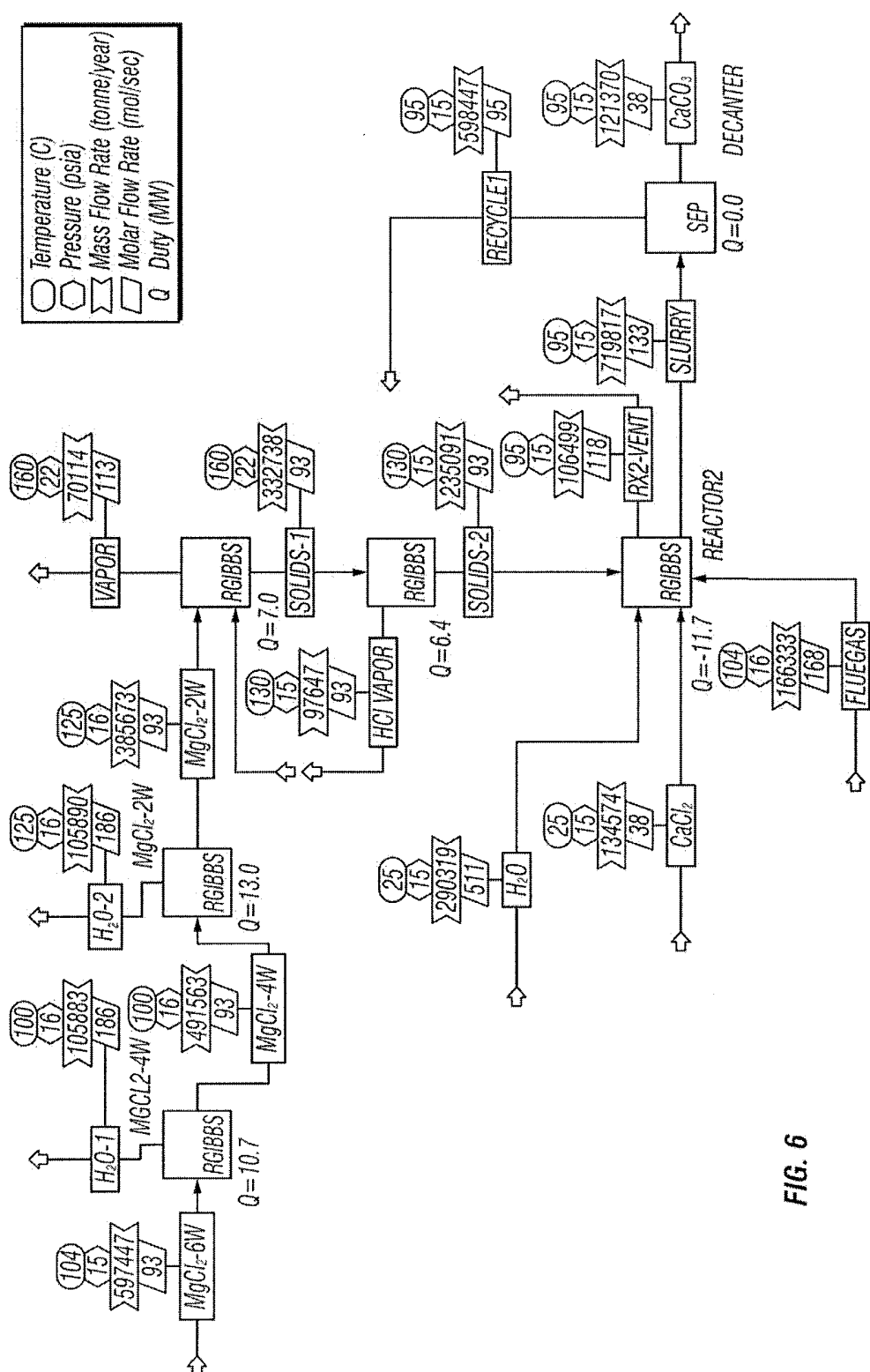


FIG. 6

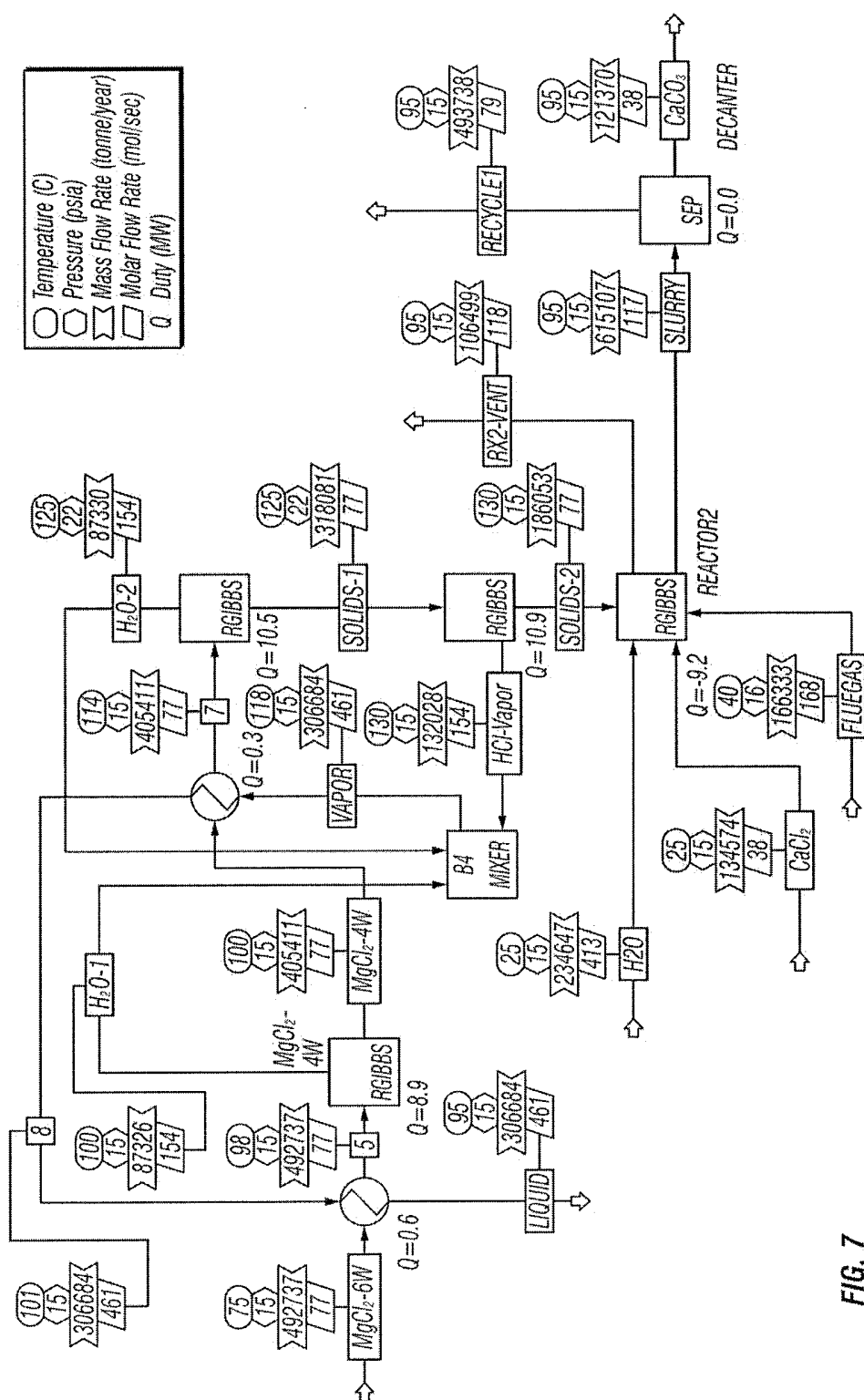


FIG. 7

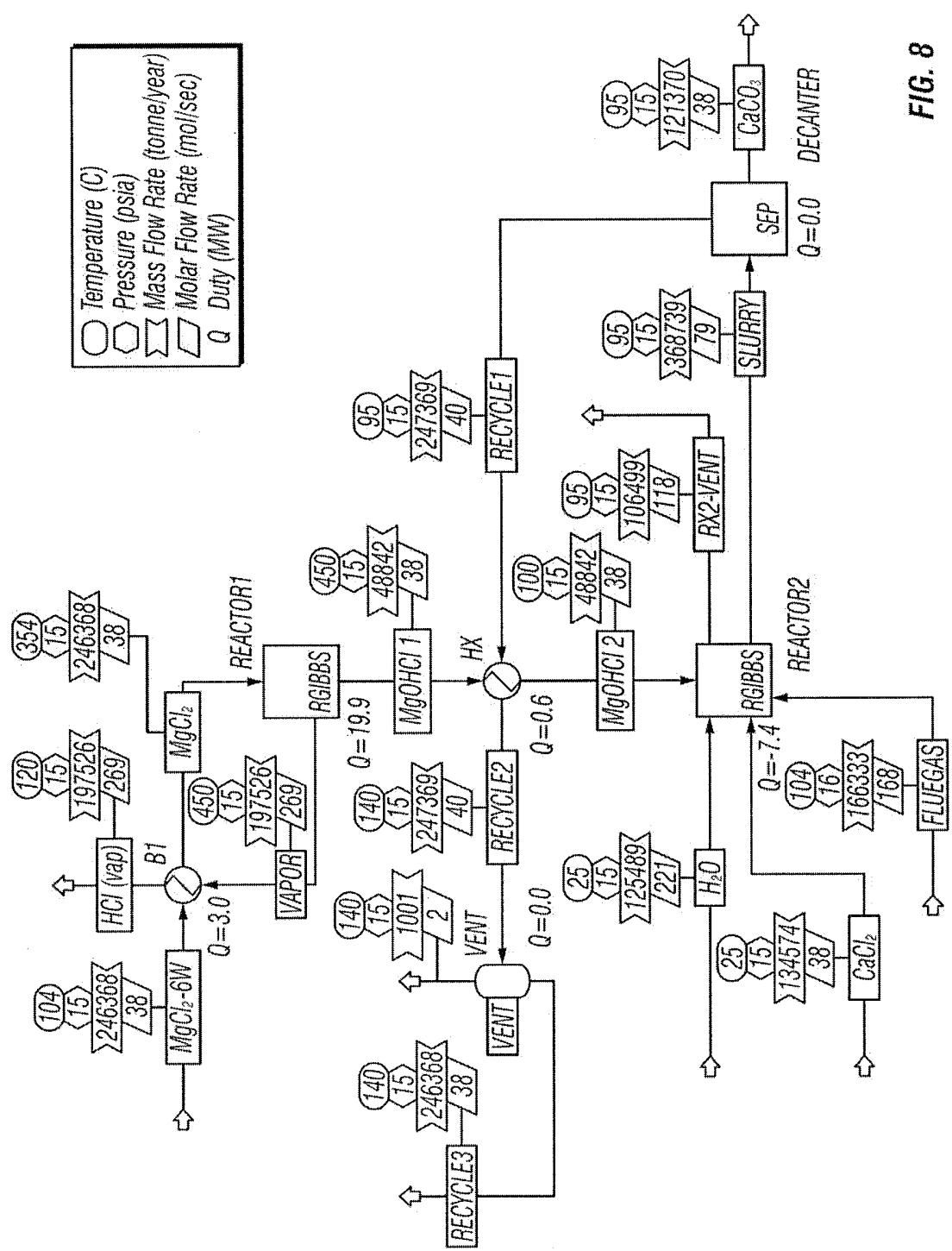


FIG. 8

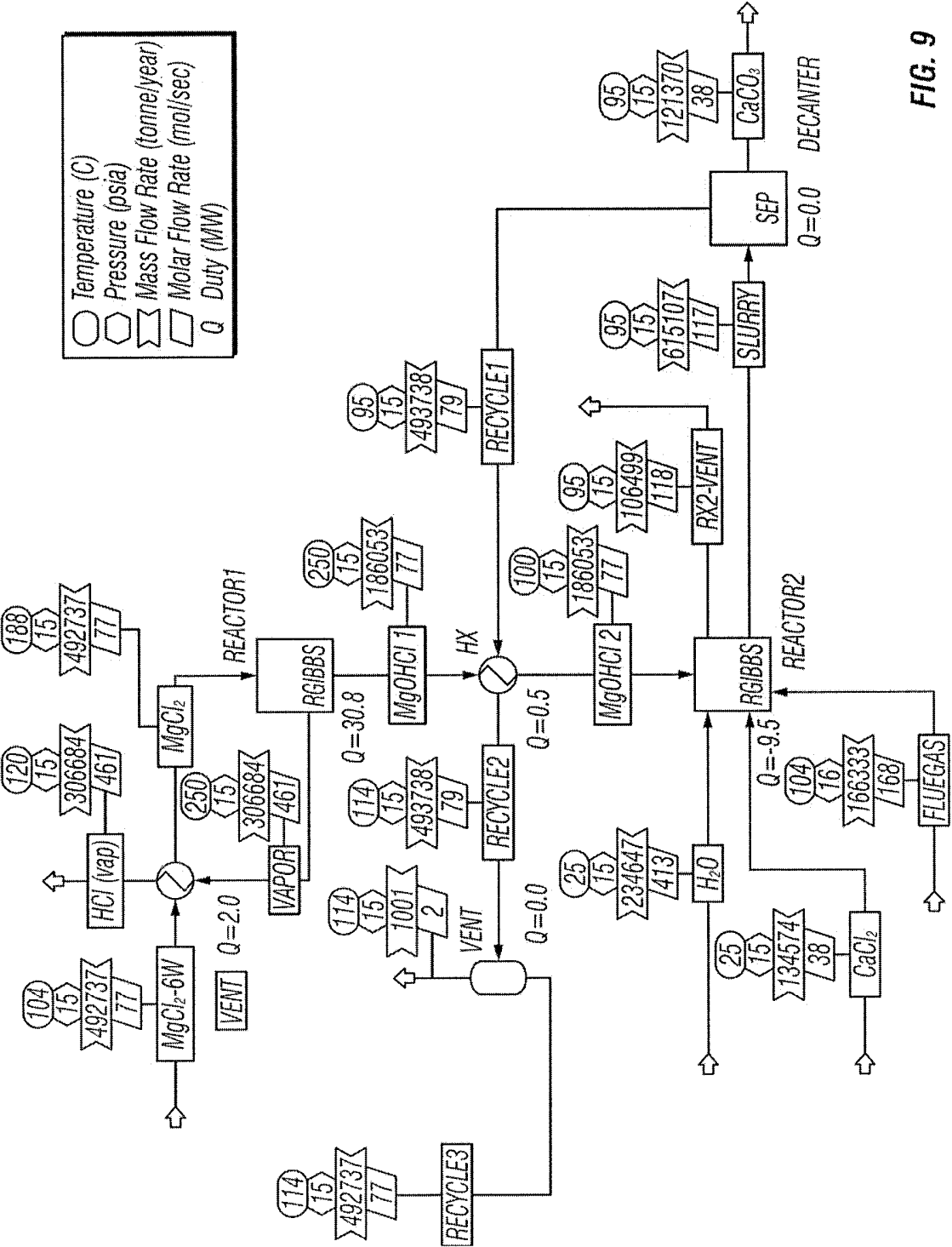


FIG. 9

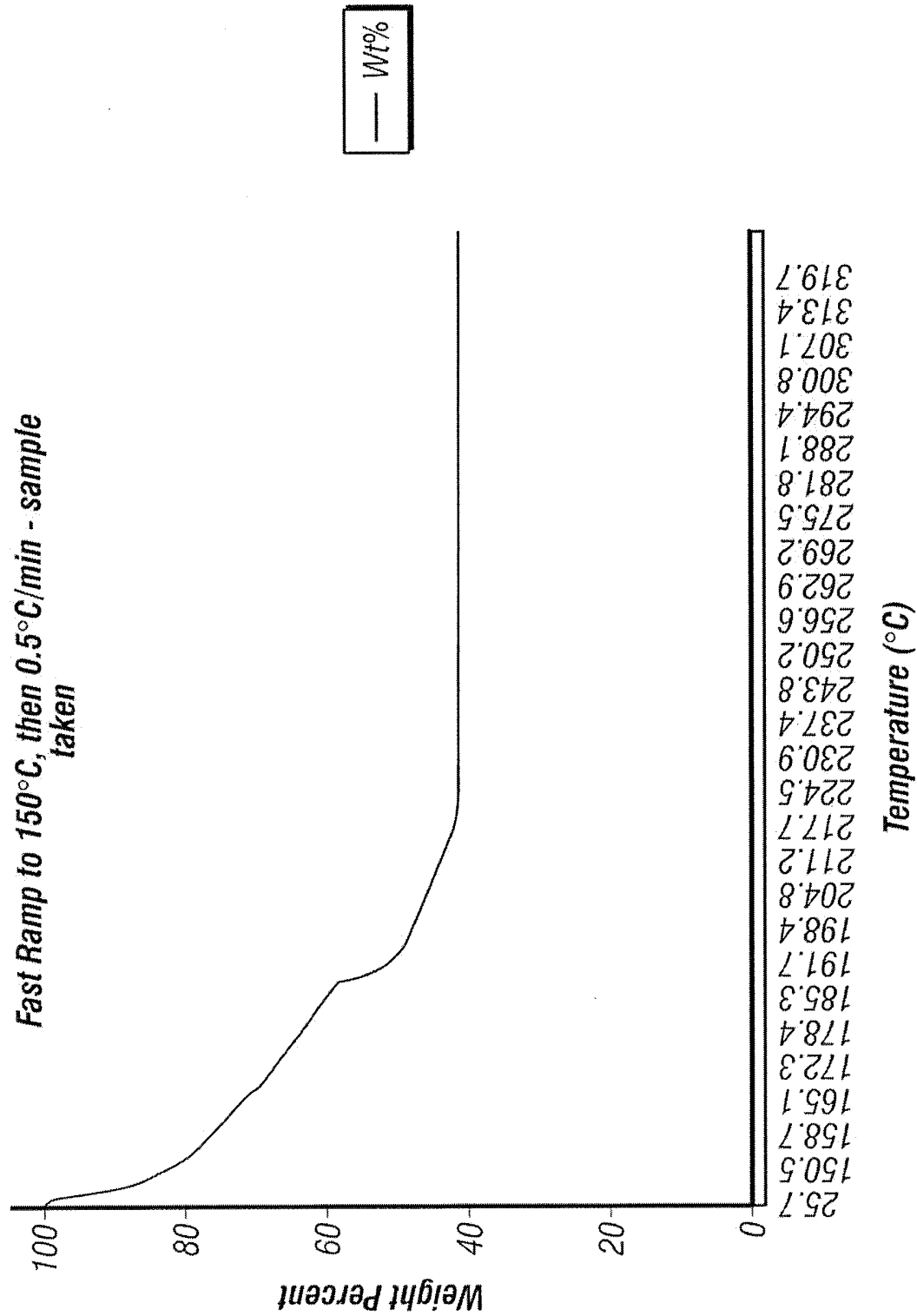


FIG. 10

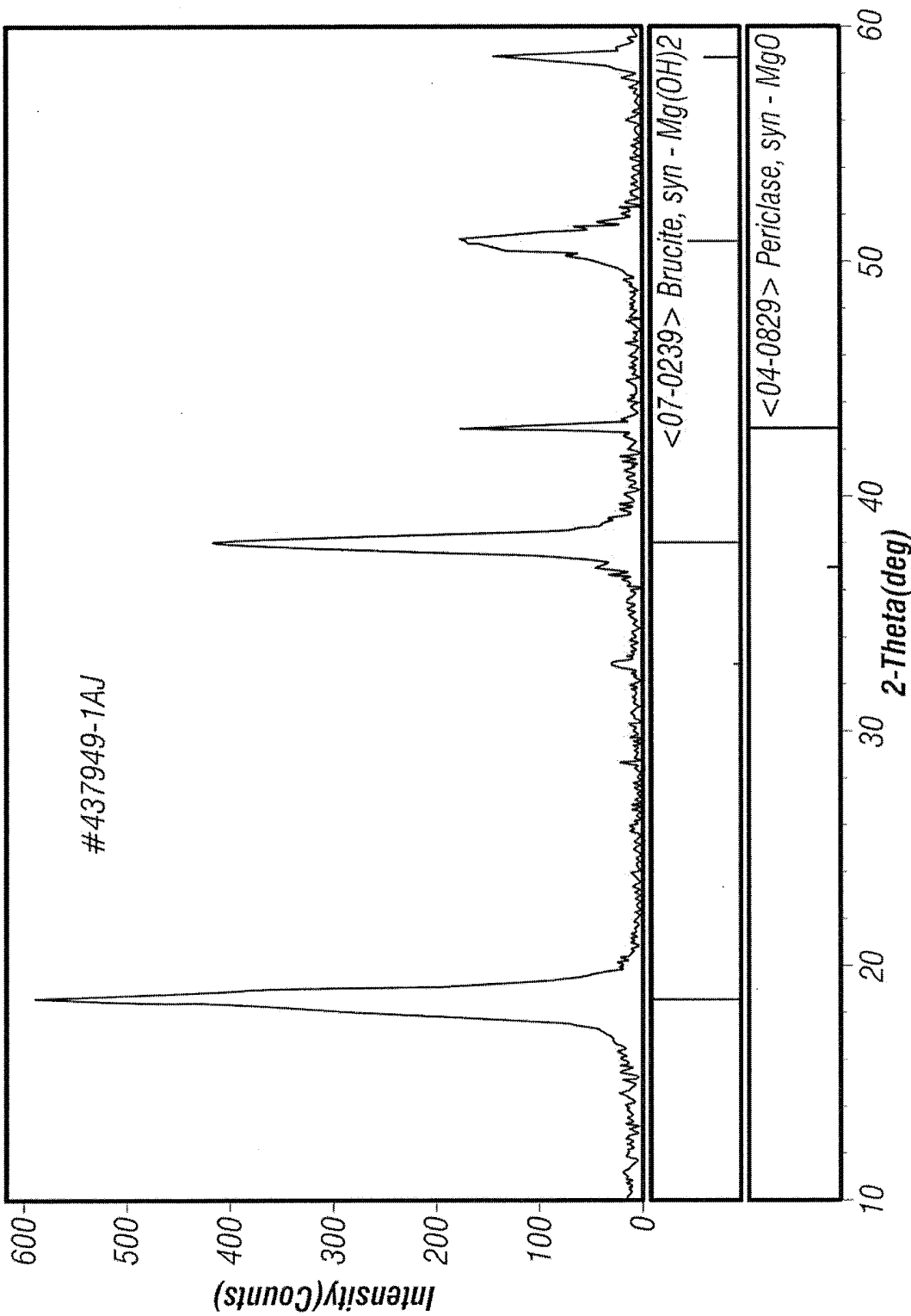


FIG. 11

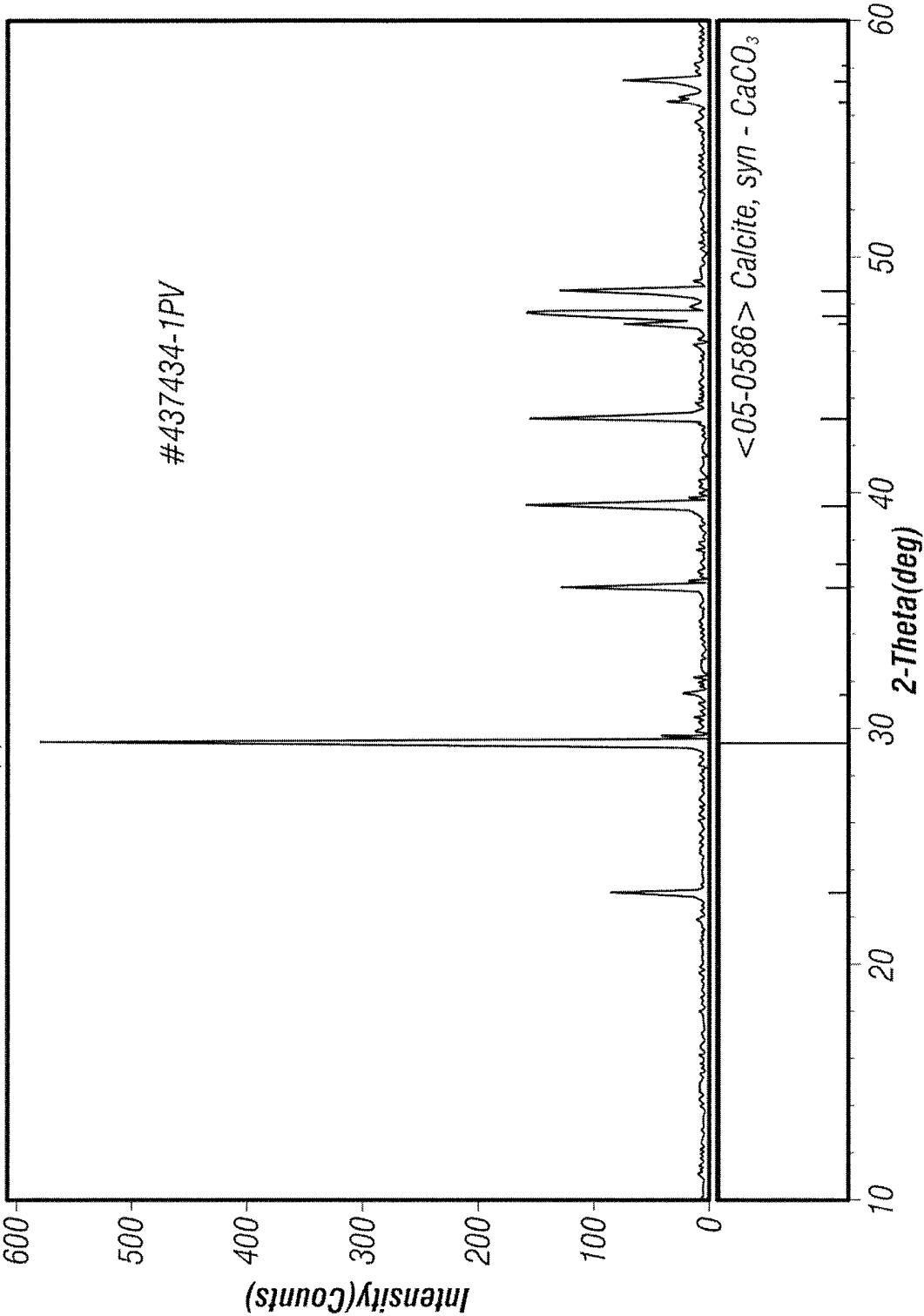


FIG. 12

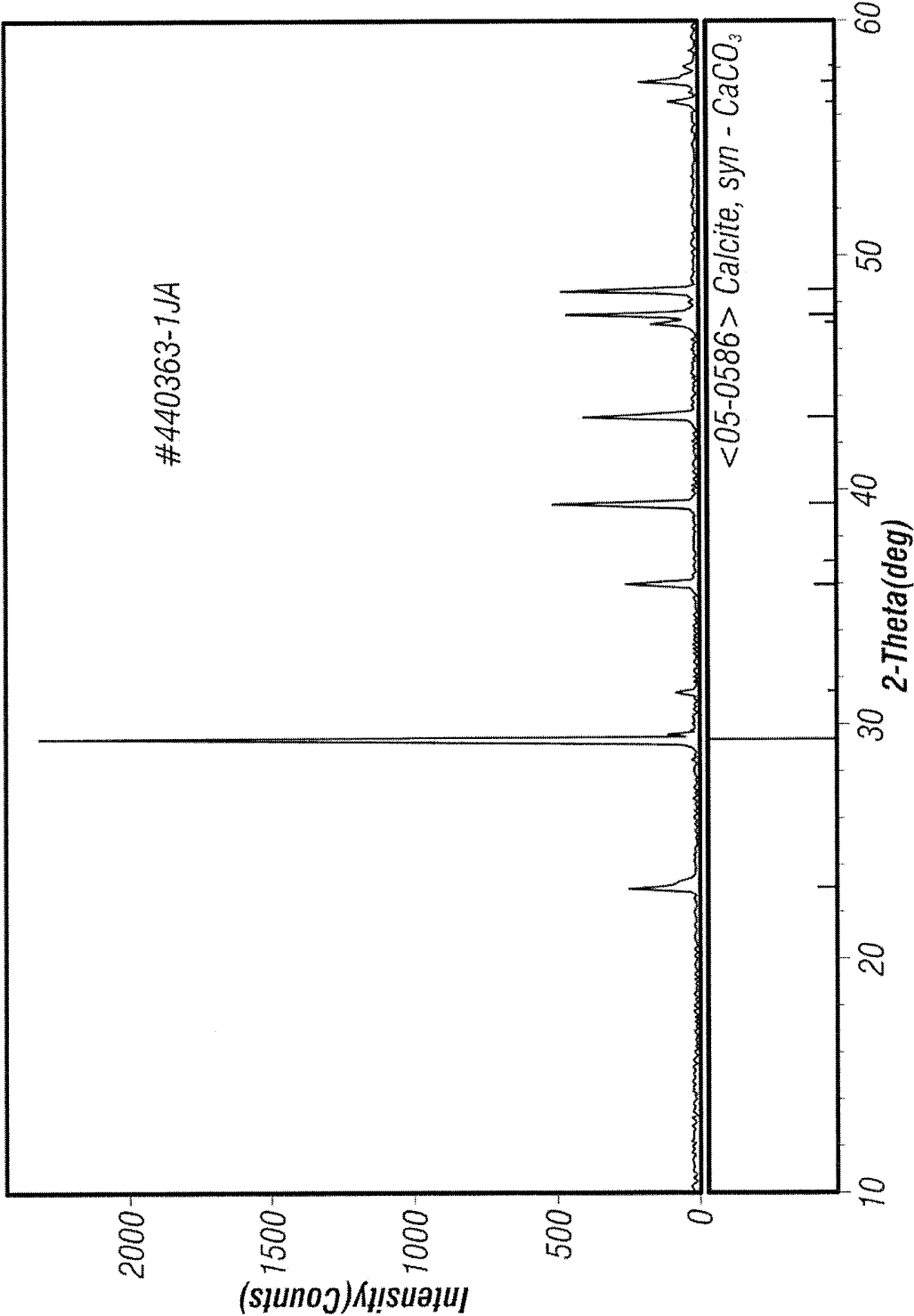


FIG. 13

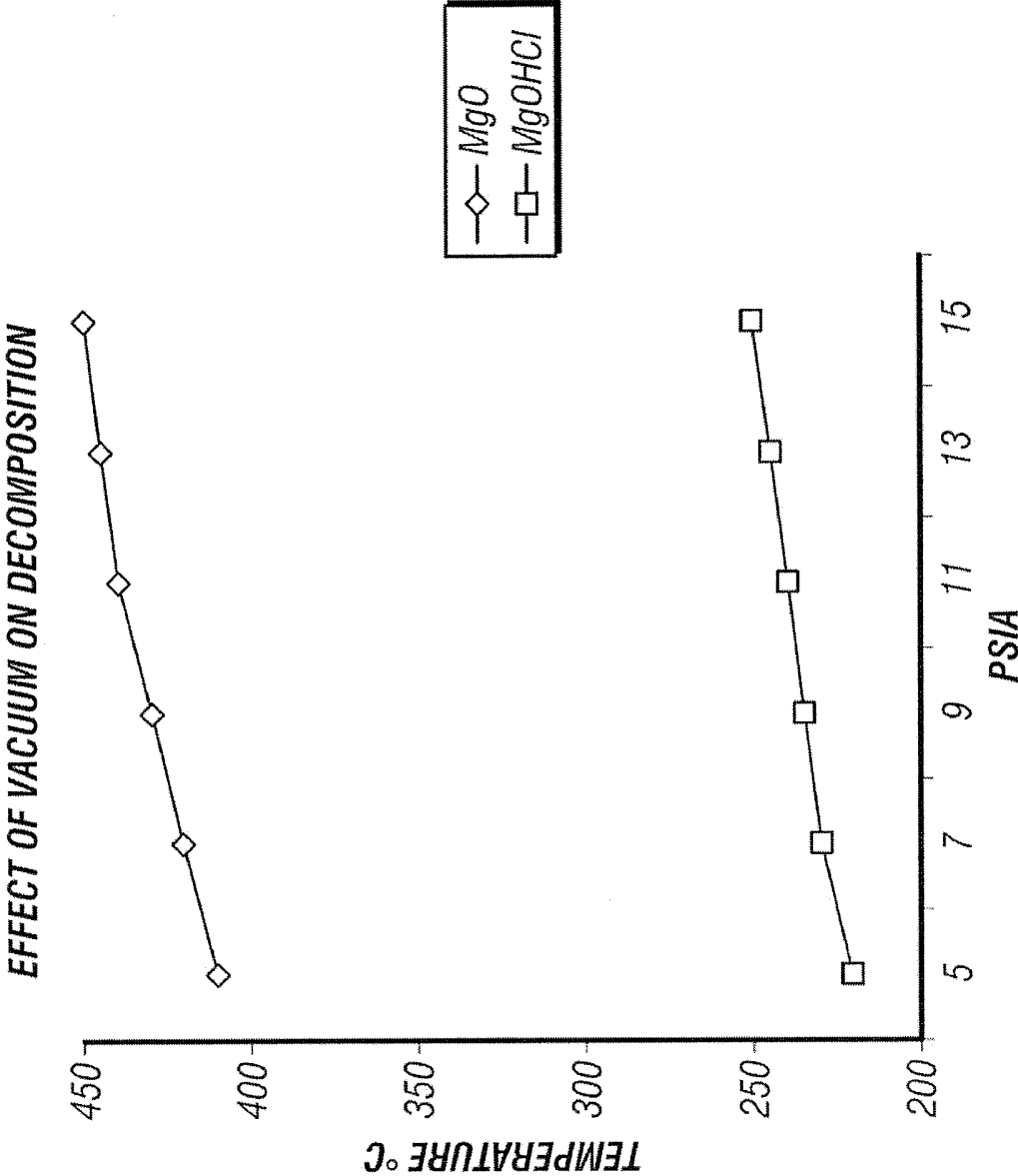


FIG. 14

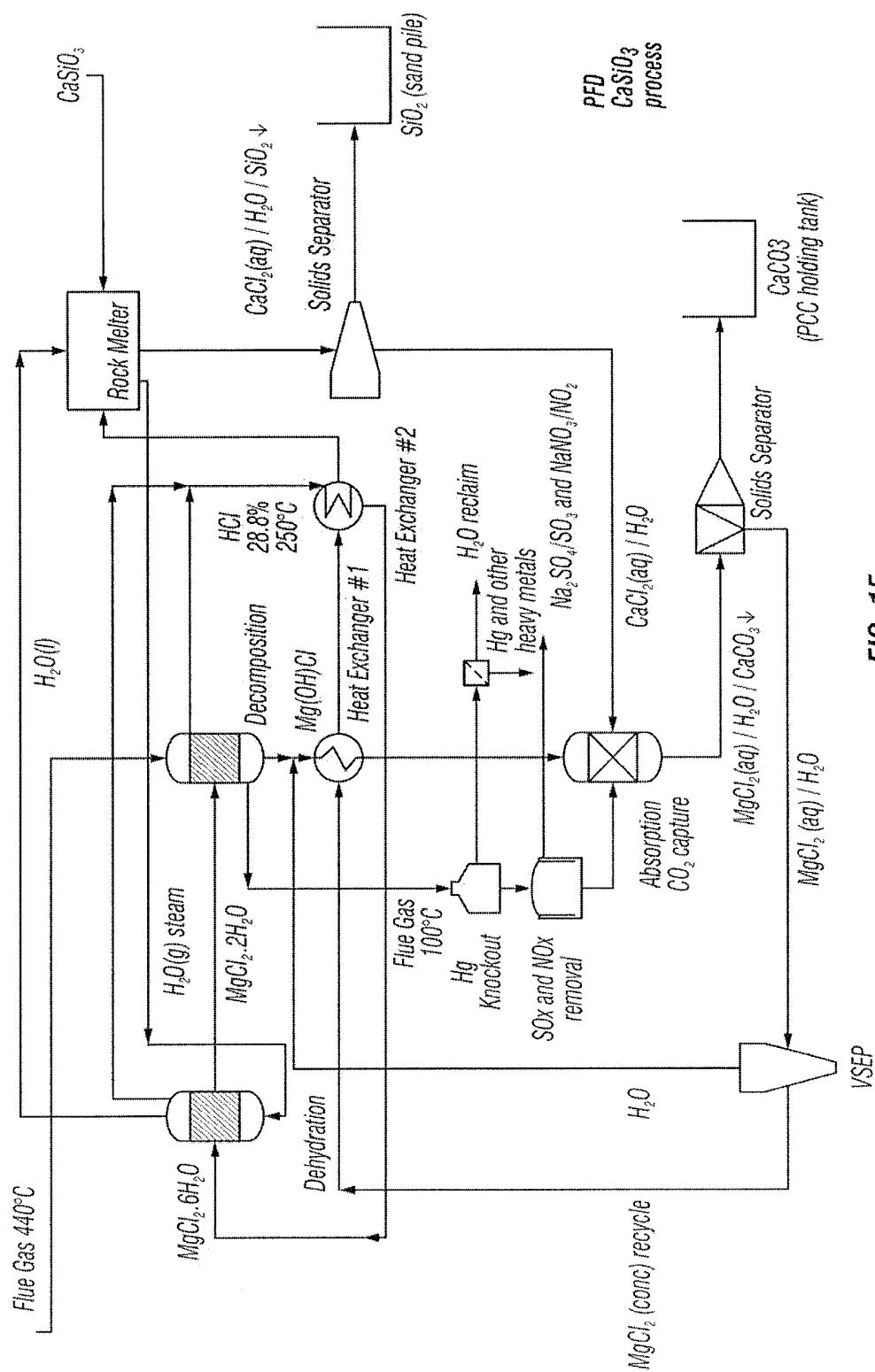
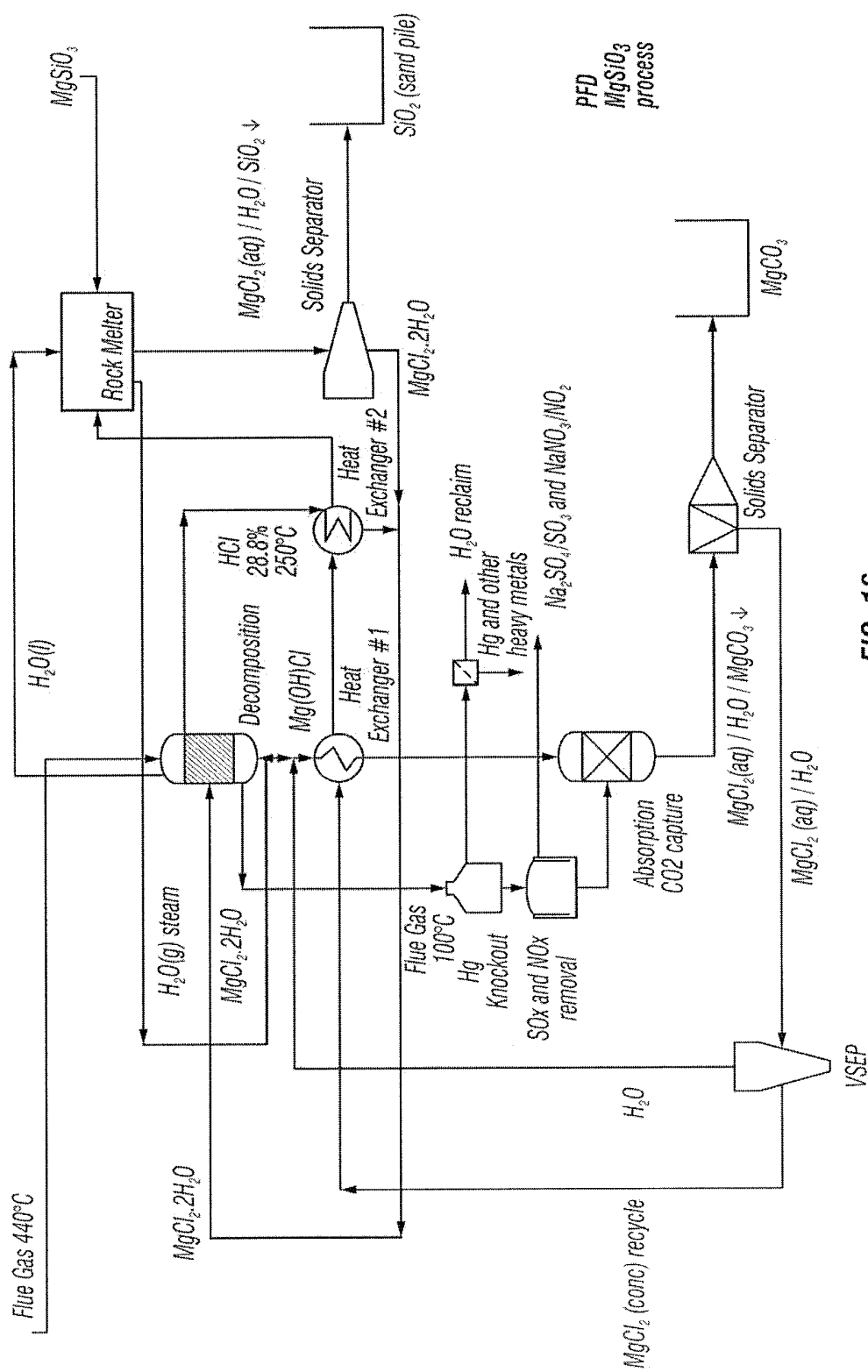


FIG. 15

PFD
CaSiO₃
process



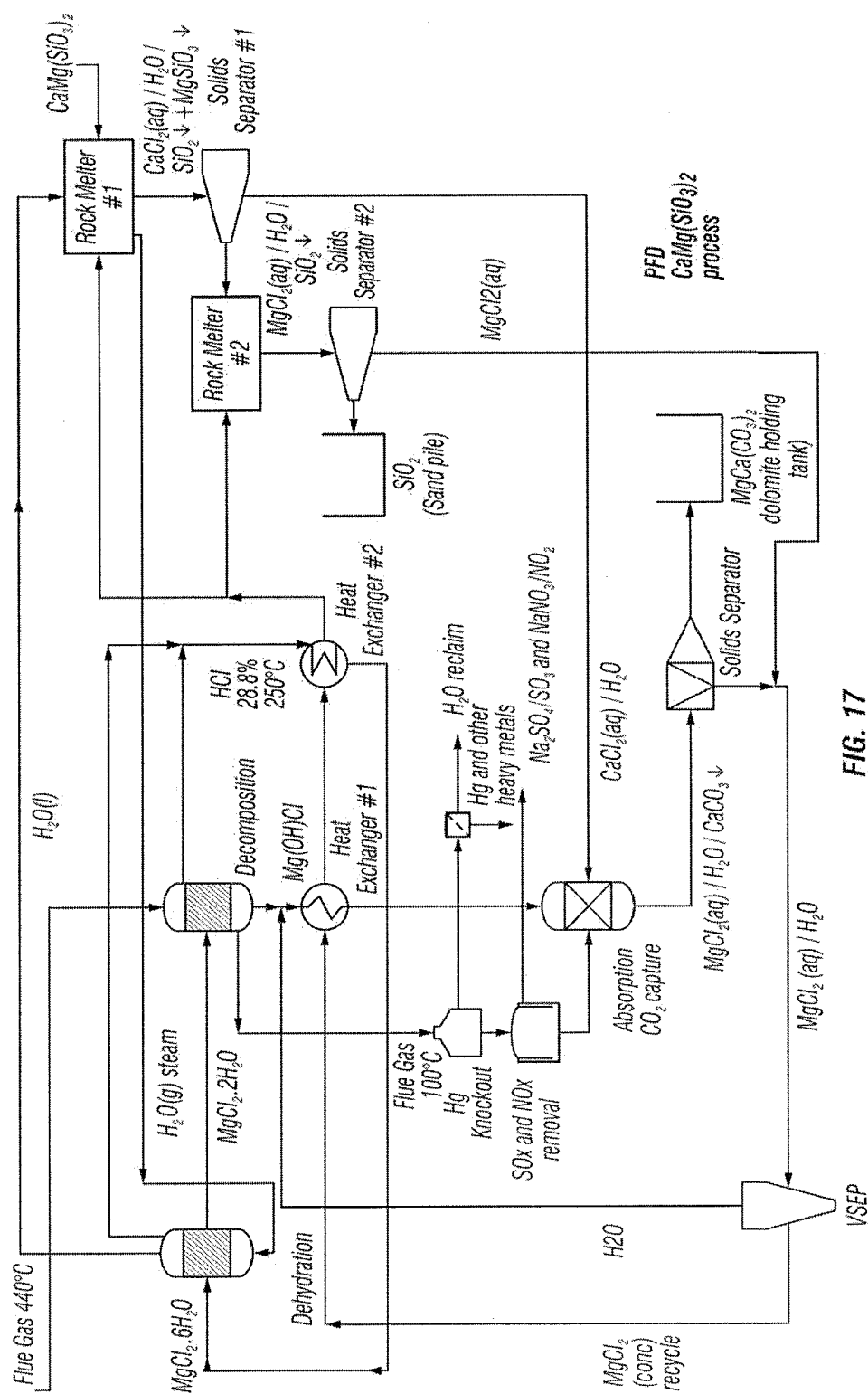
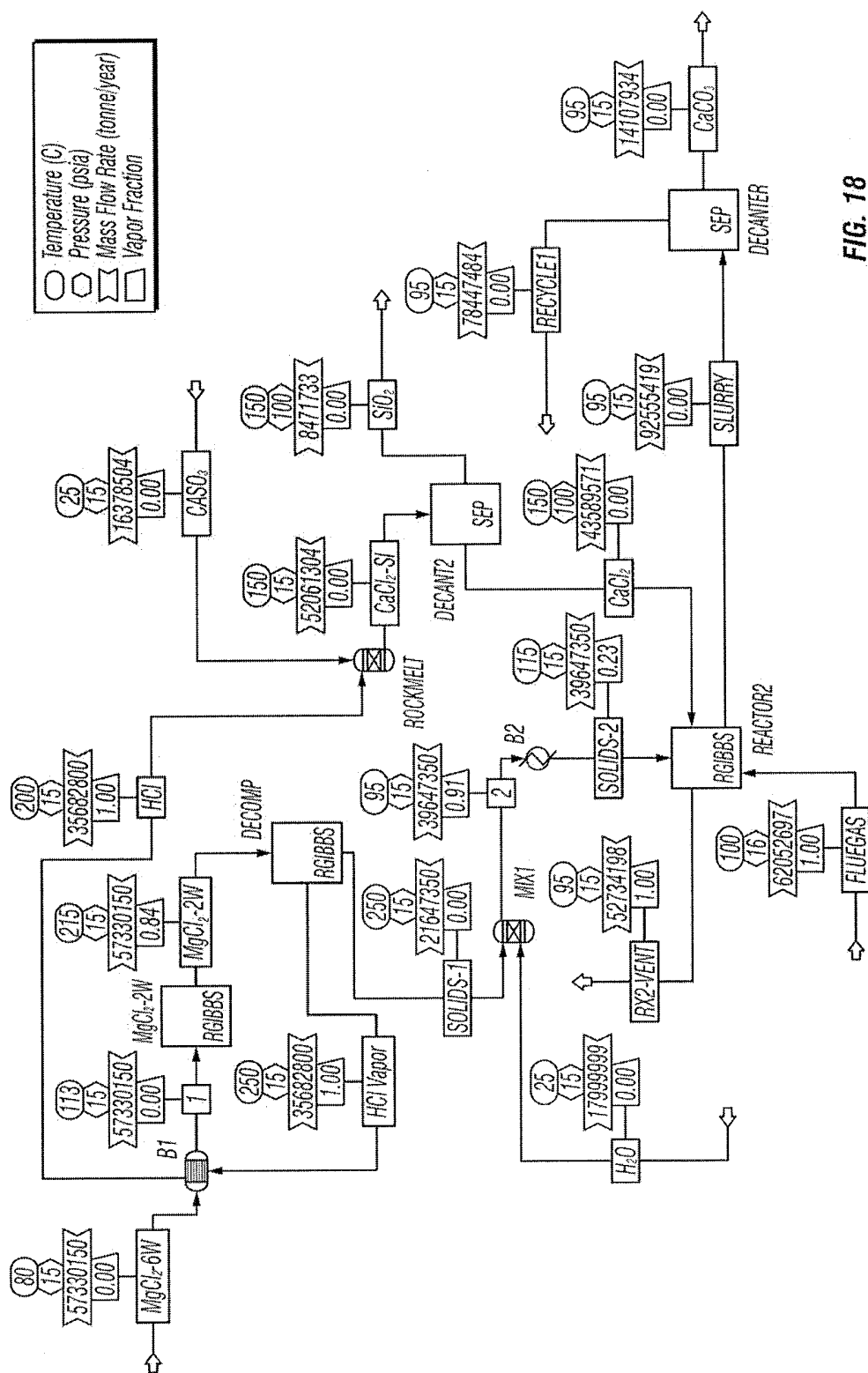


FIG. 17



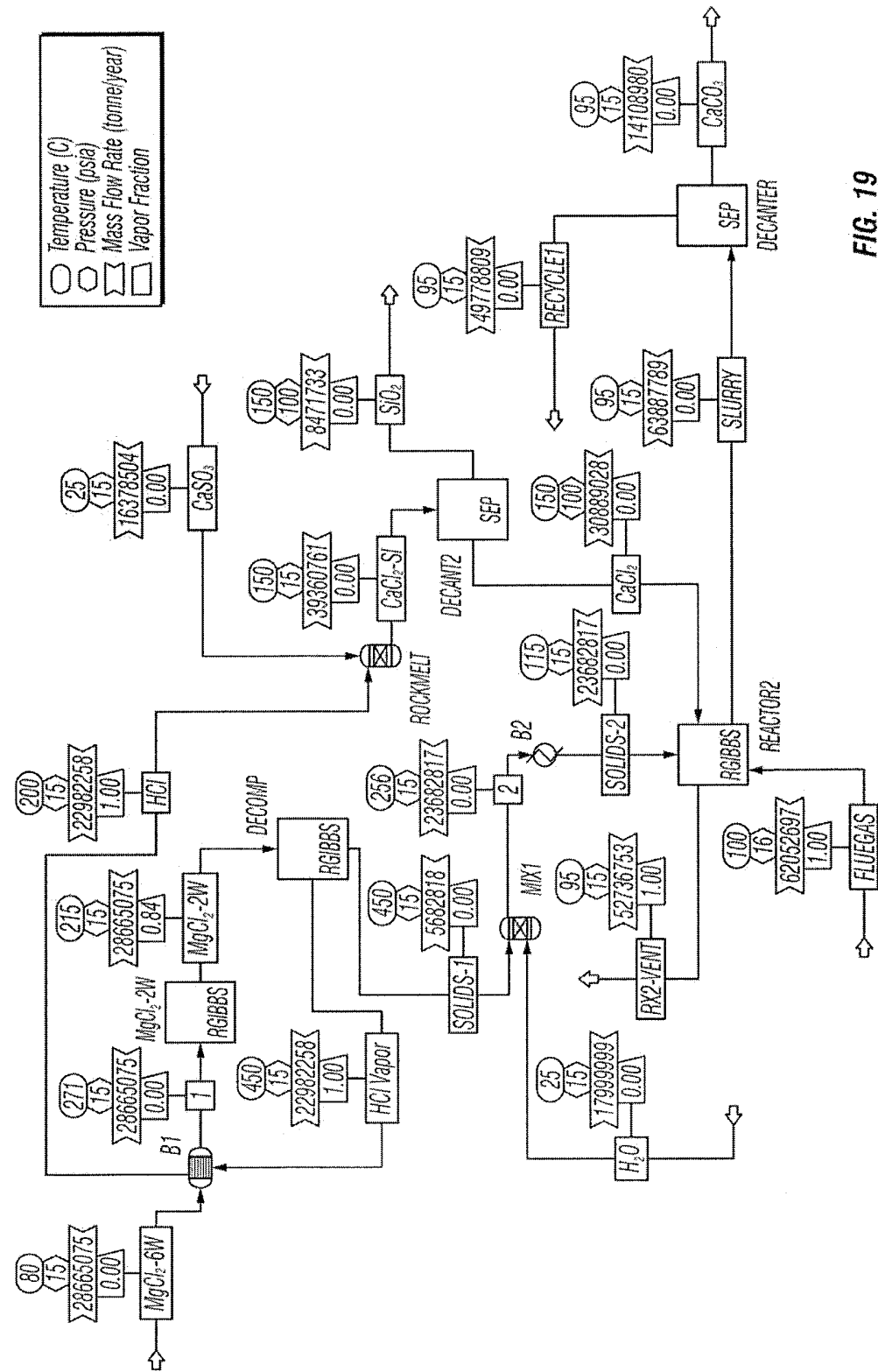


FIG. 19

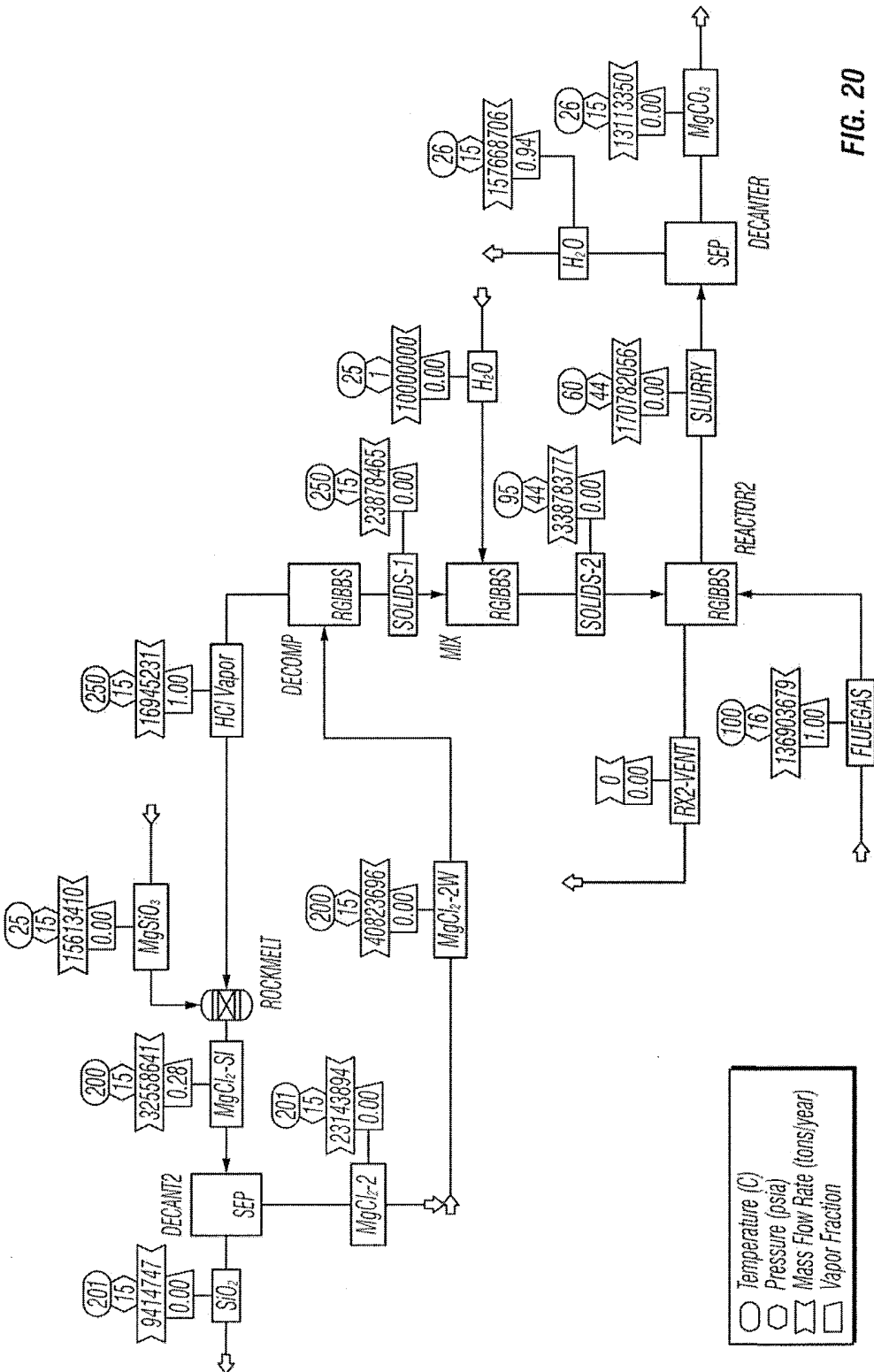


FIG. 20

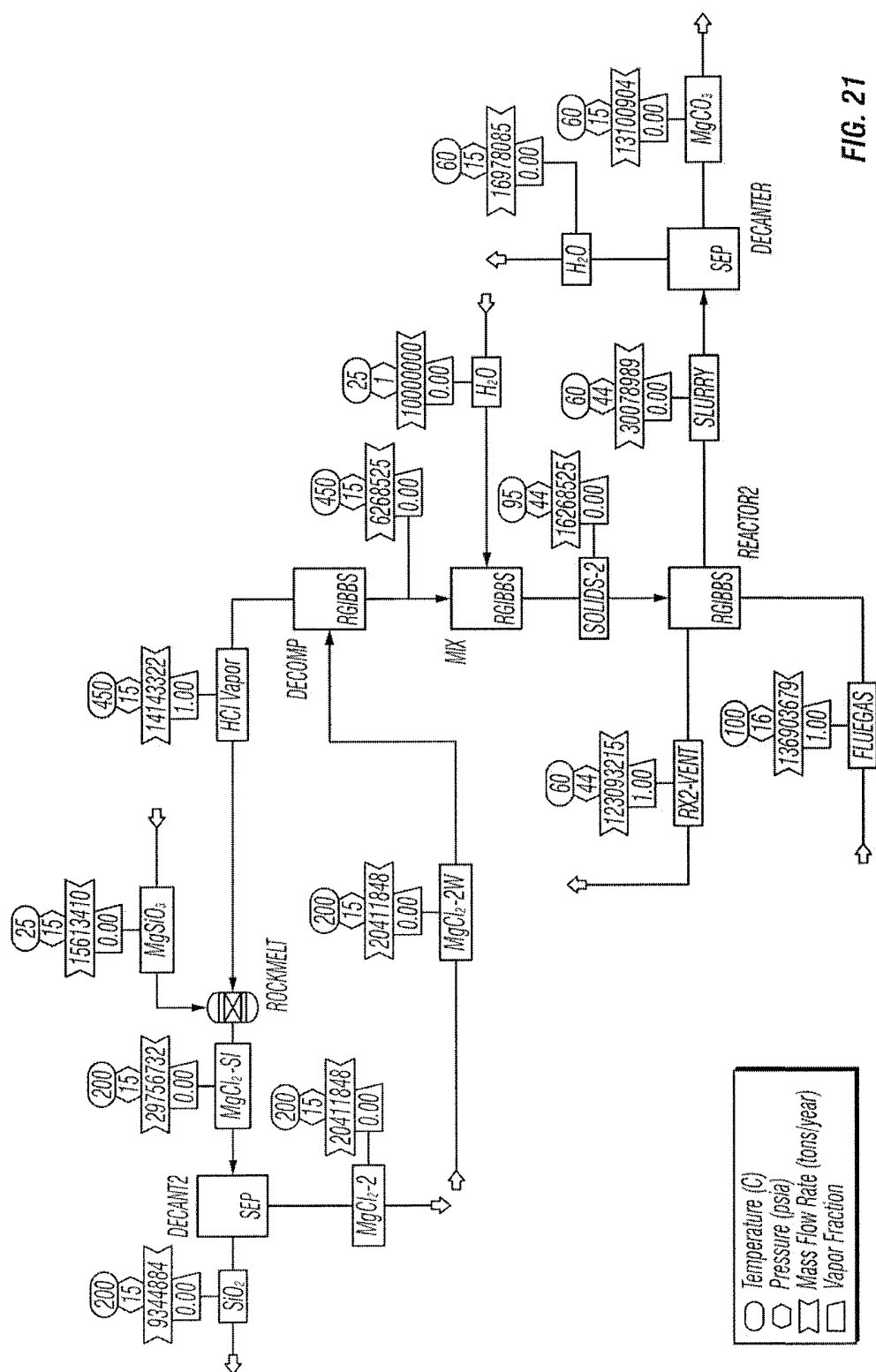


FIG. 27

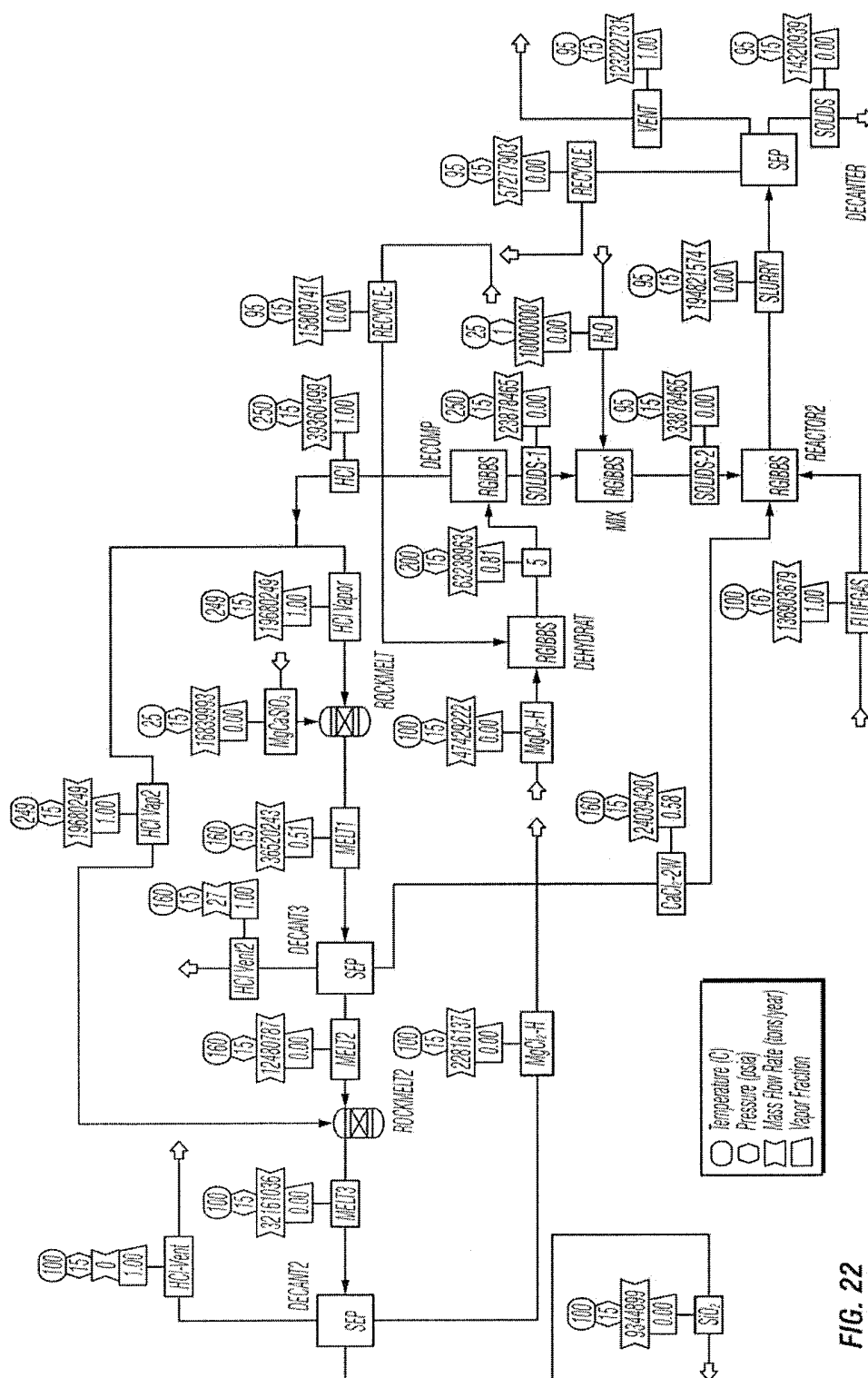


FIG. 22

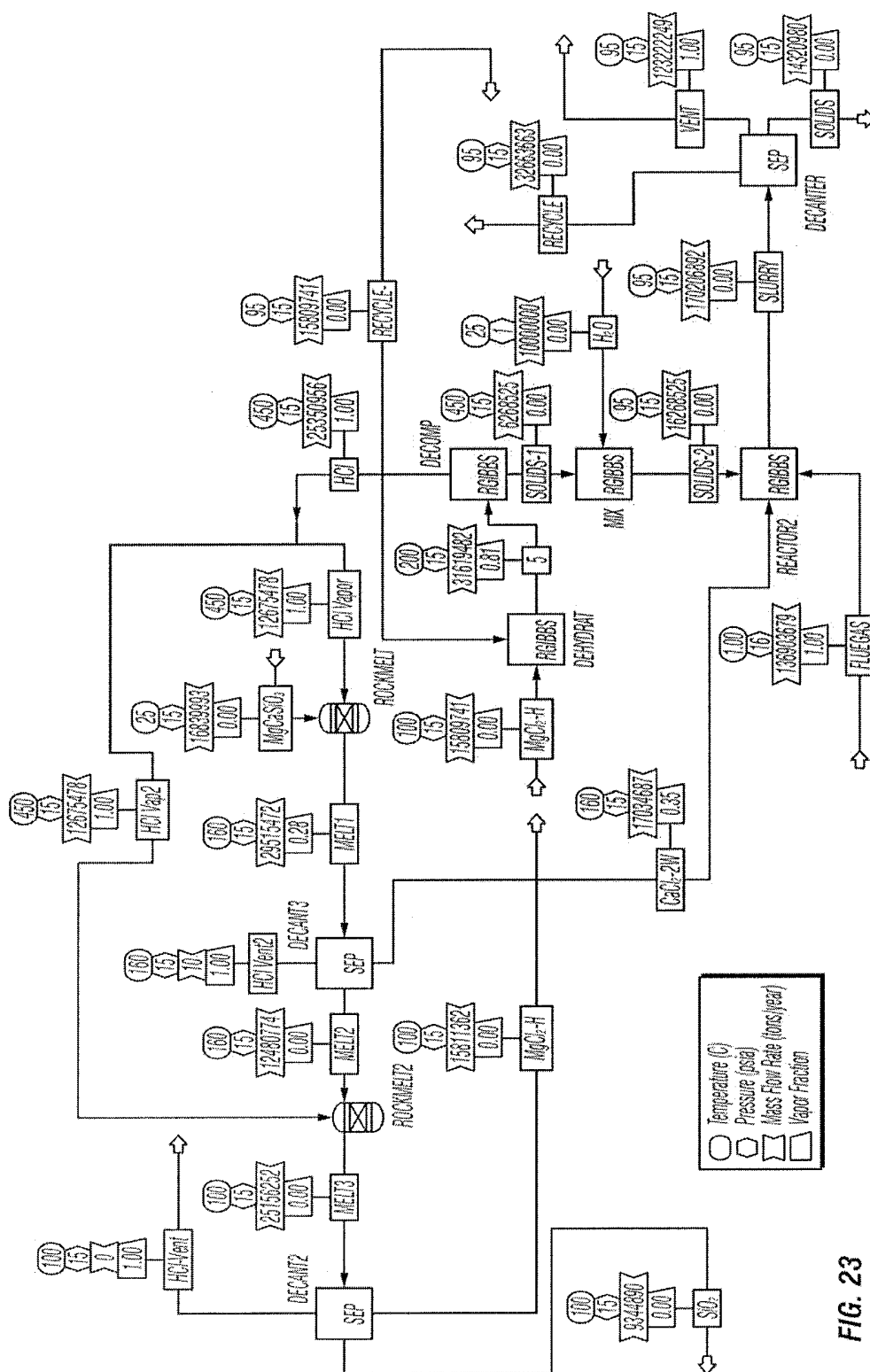


FIG. 23

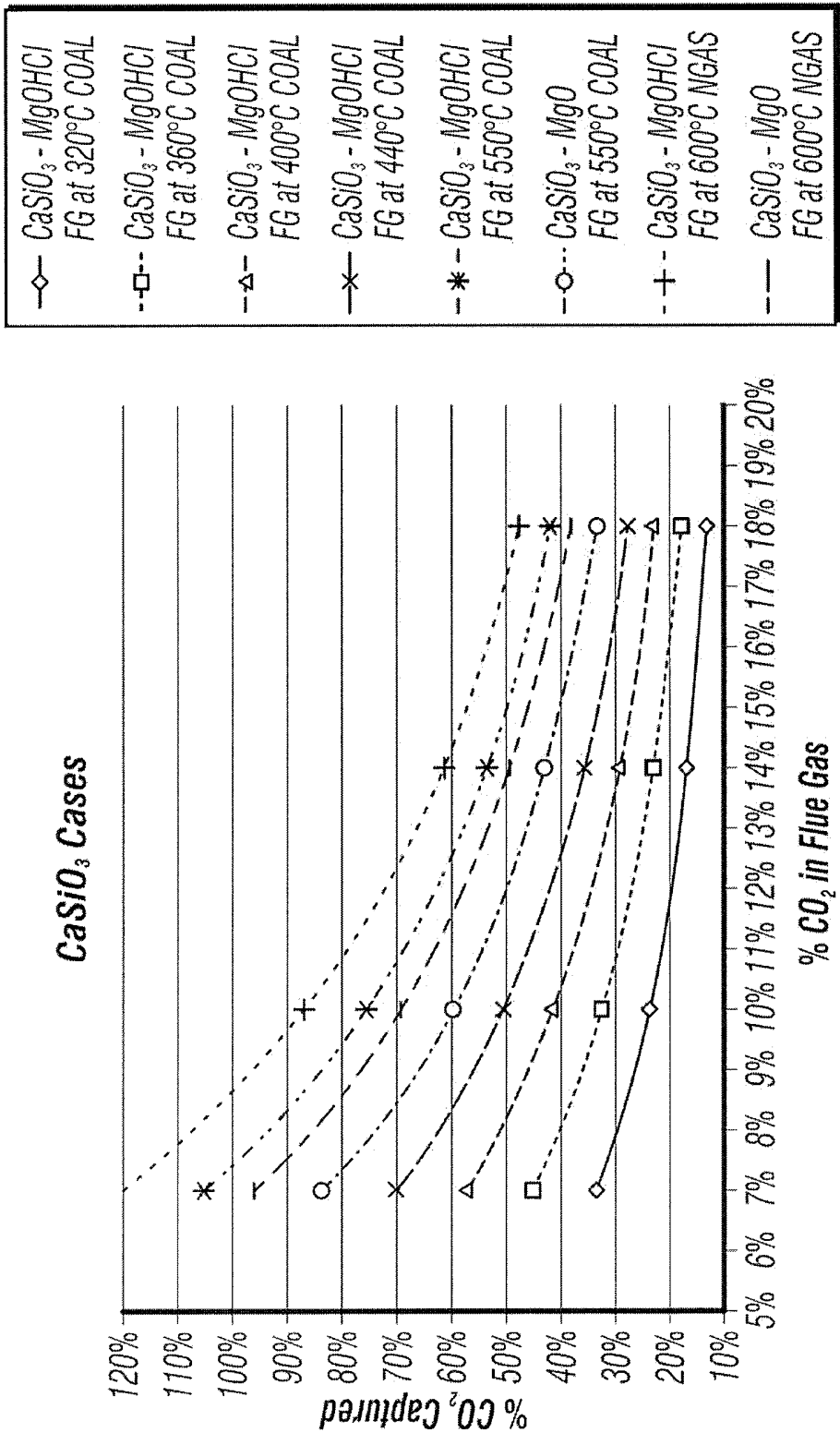


FIG. 24

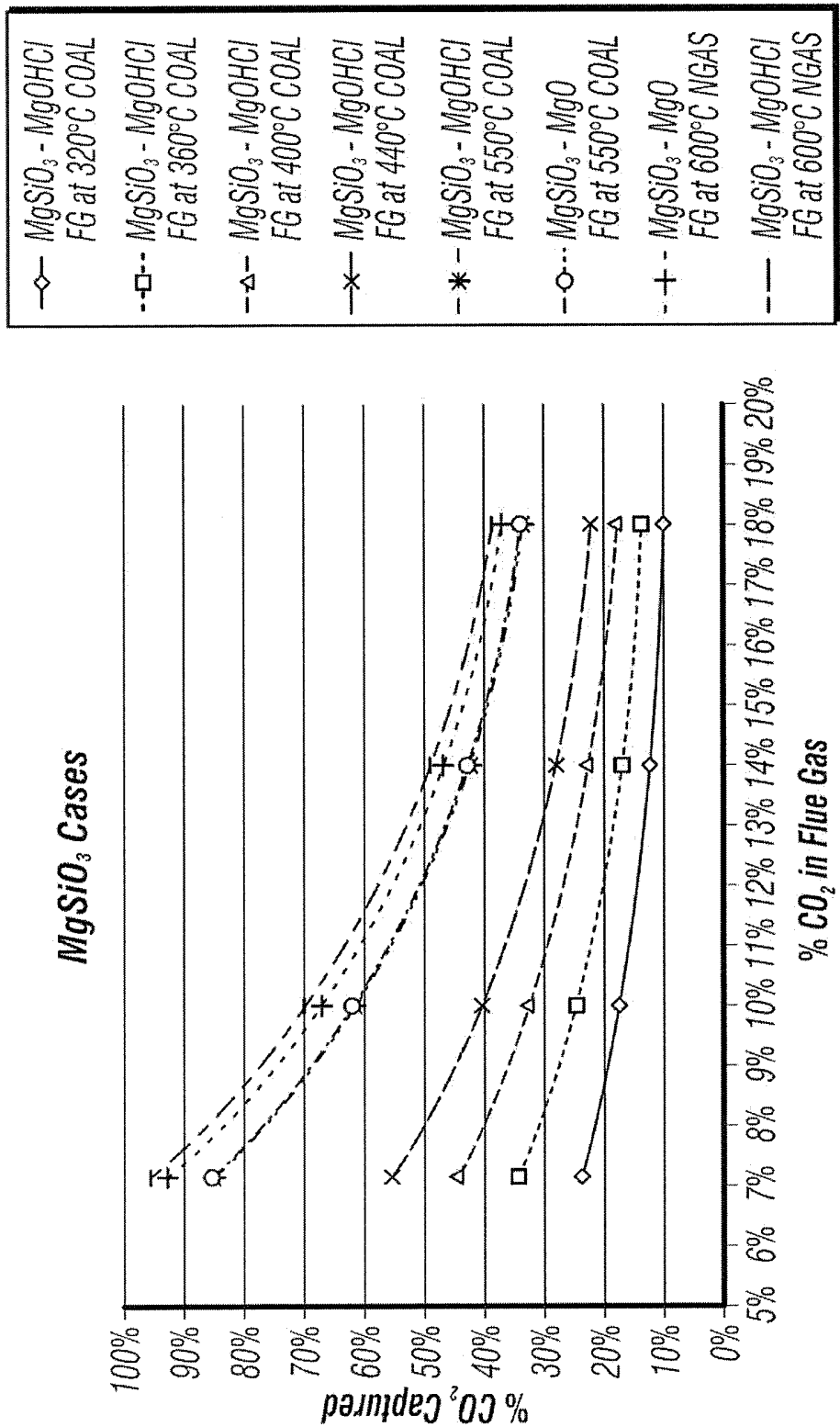


FIG. 25

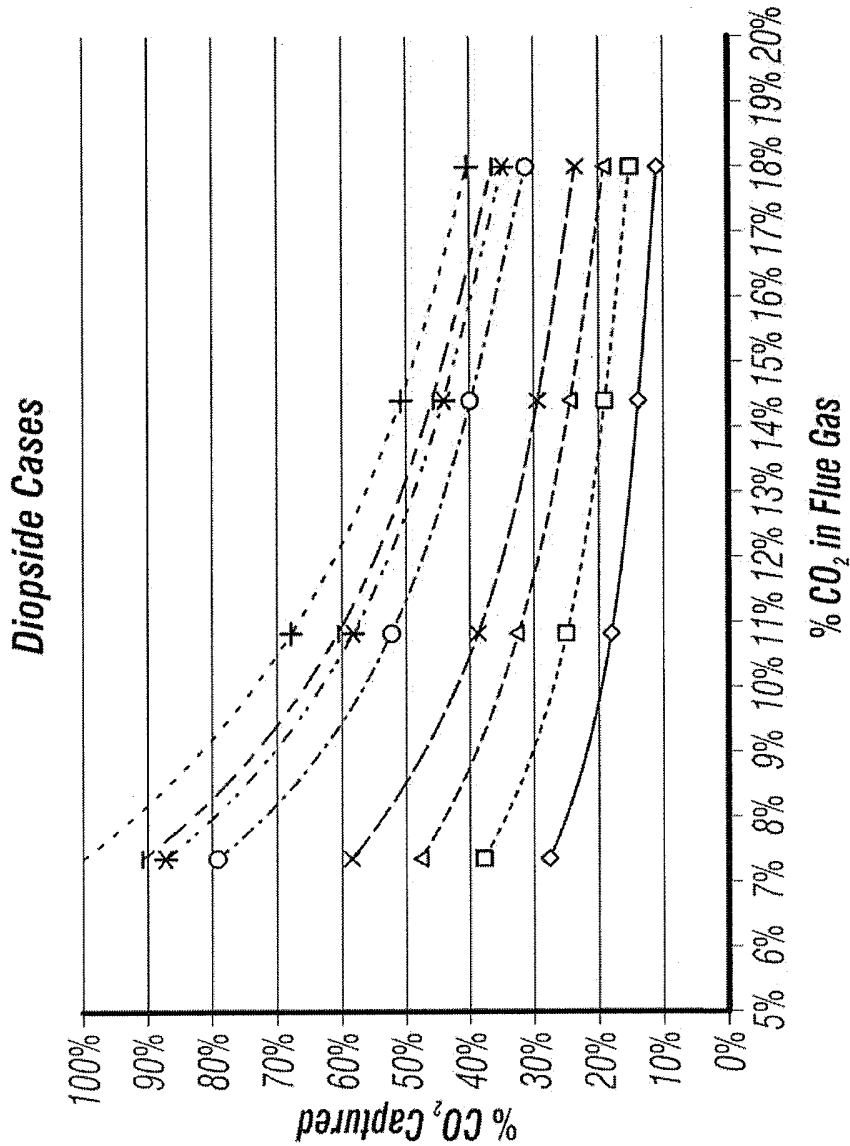
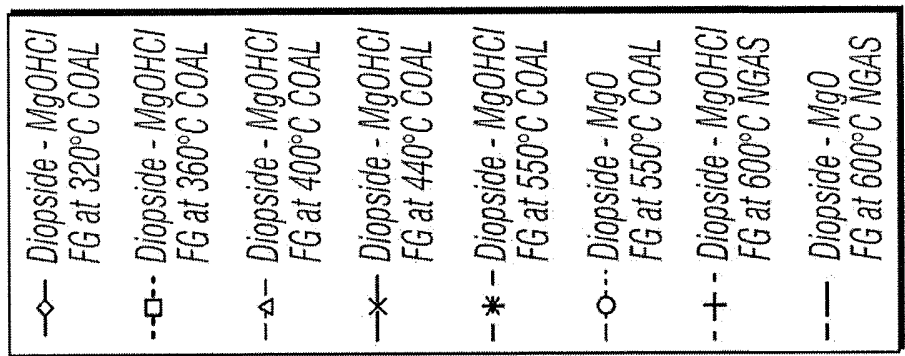


FIG. 26

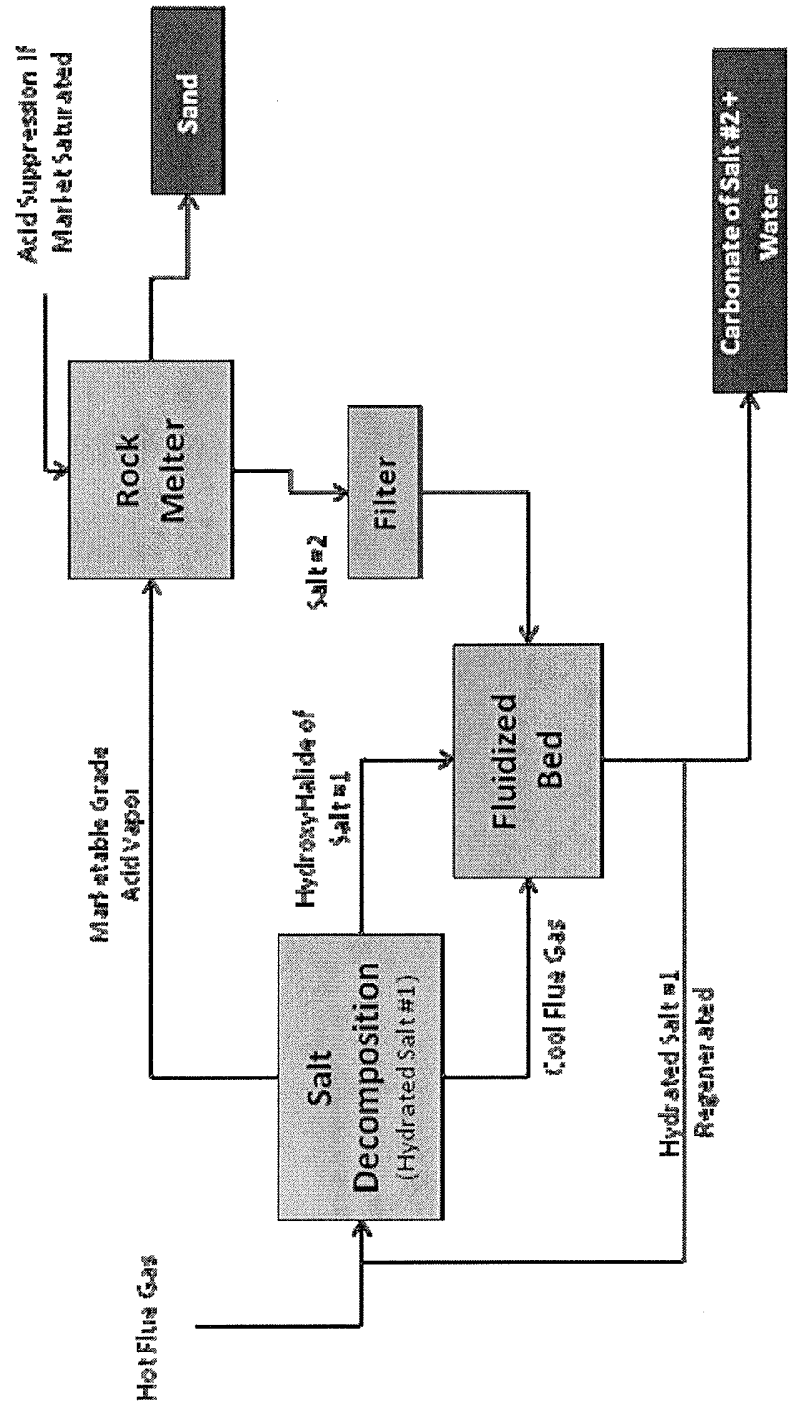


FIG. 27

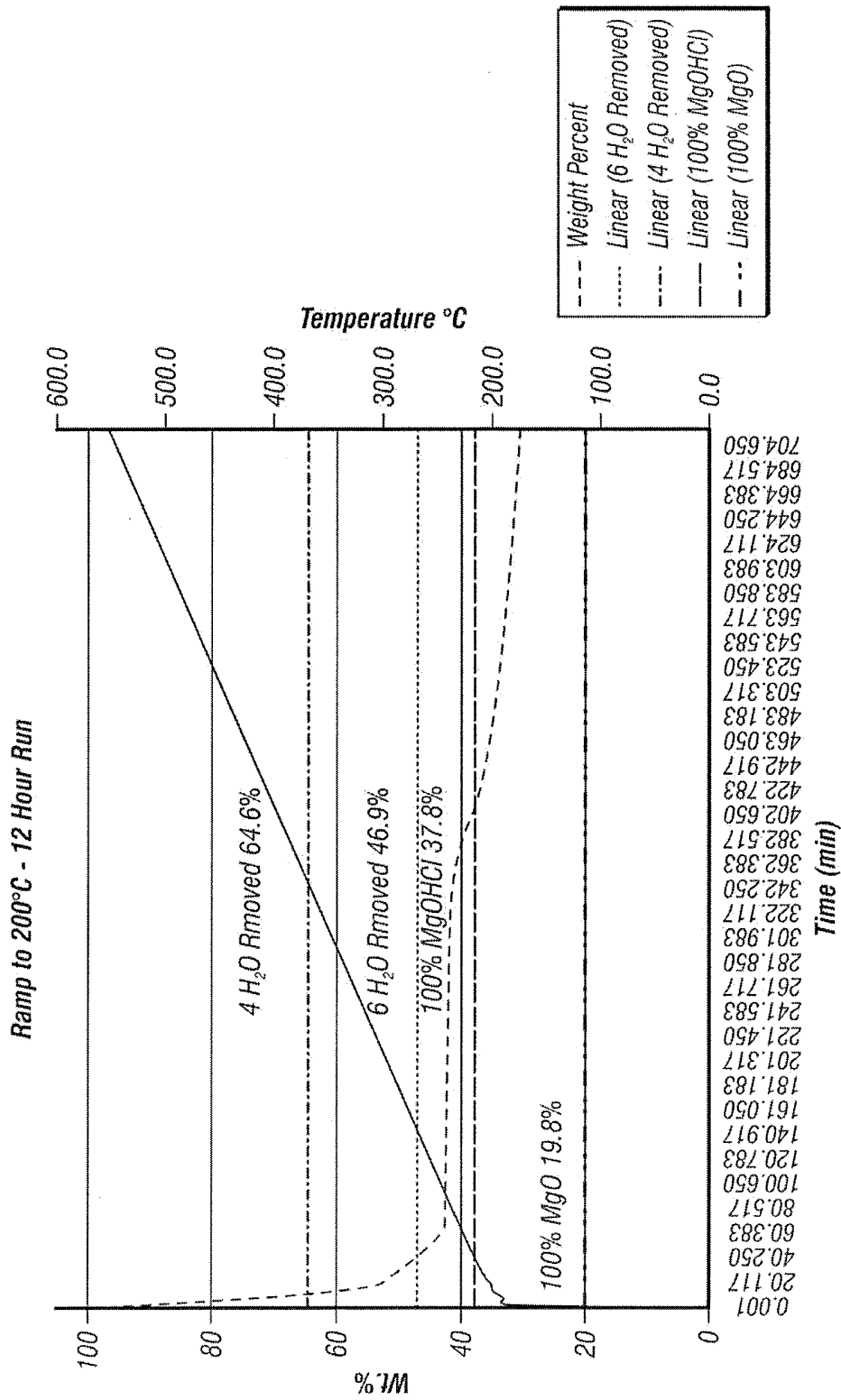


FIG. 28

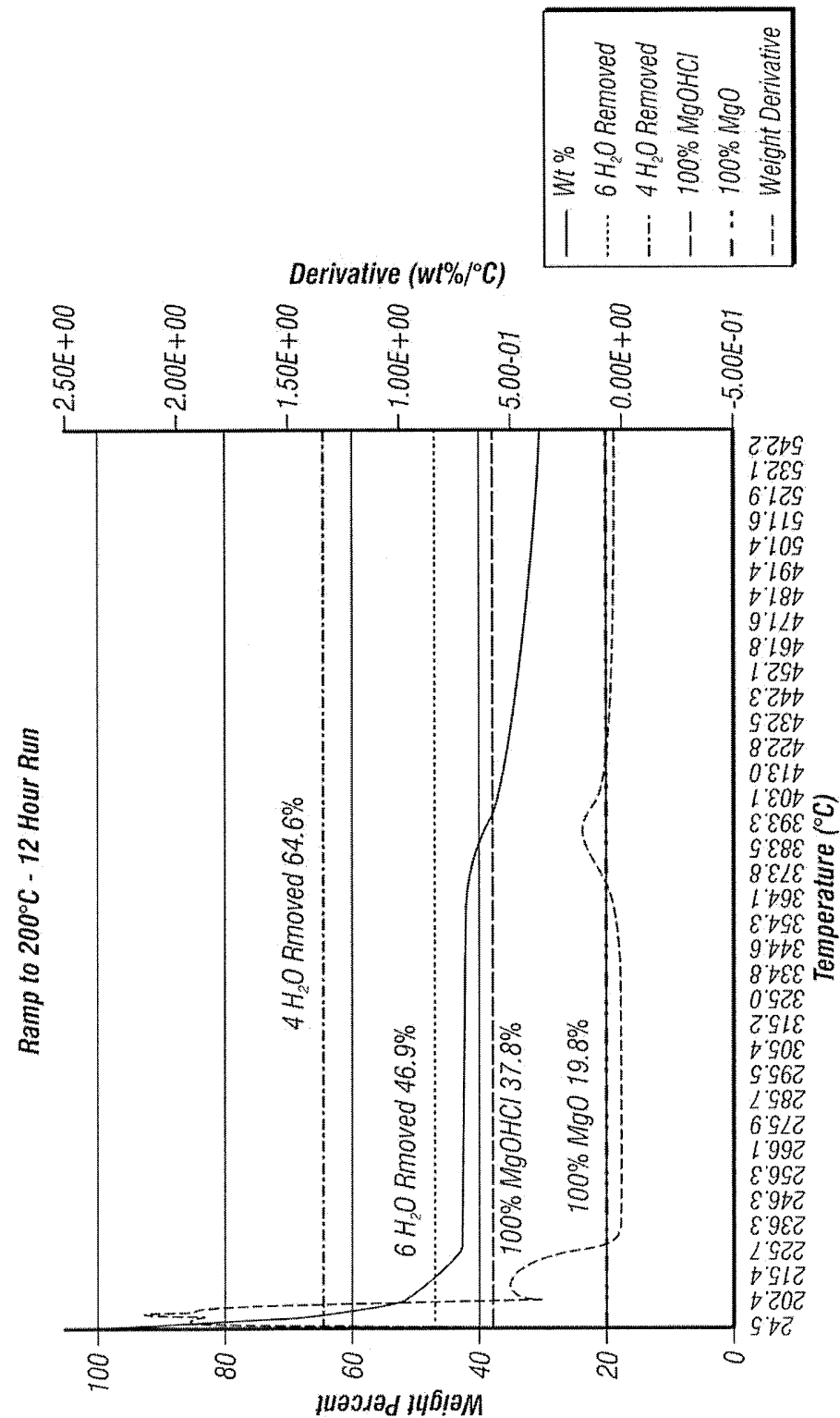


FIG. 29

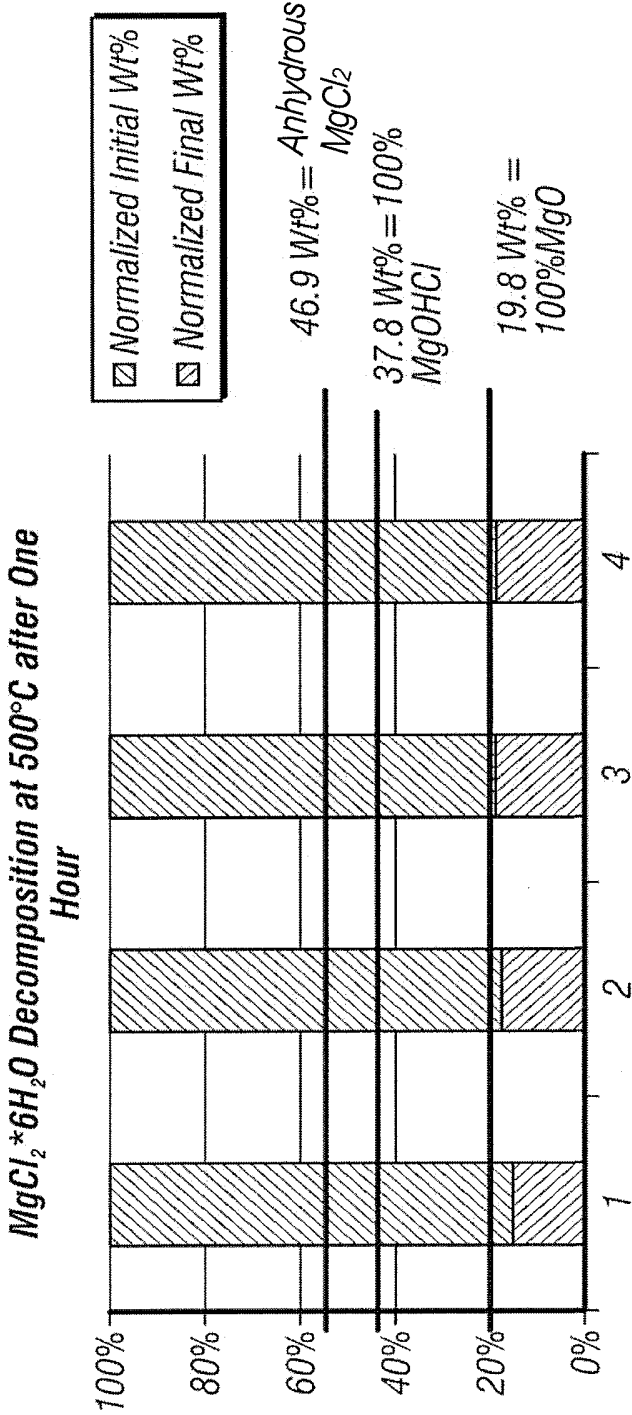


FIG. 30

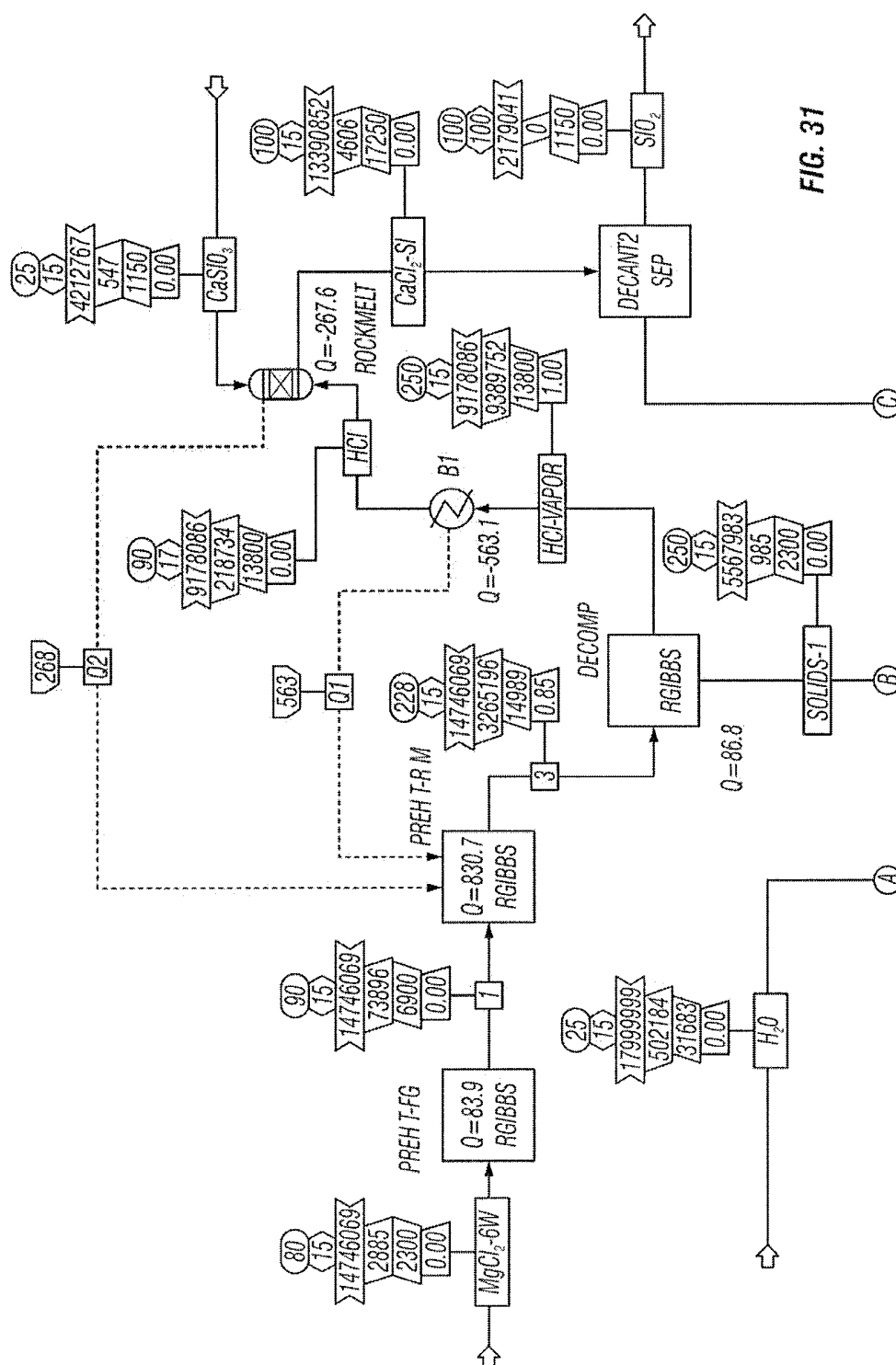


FIG. 31

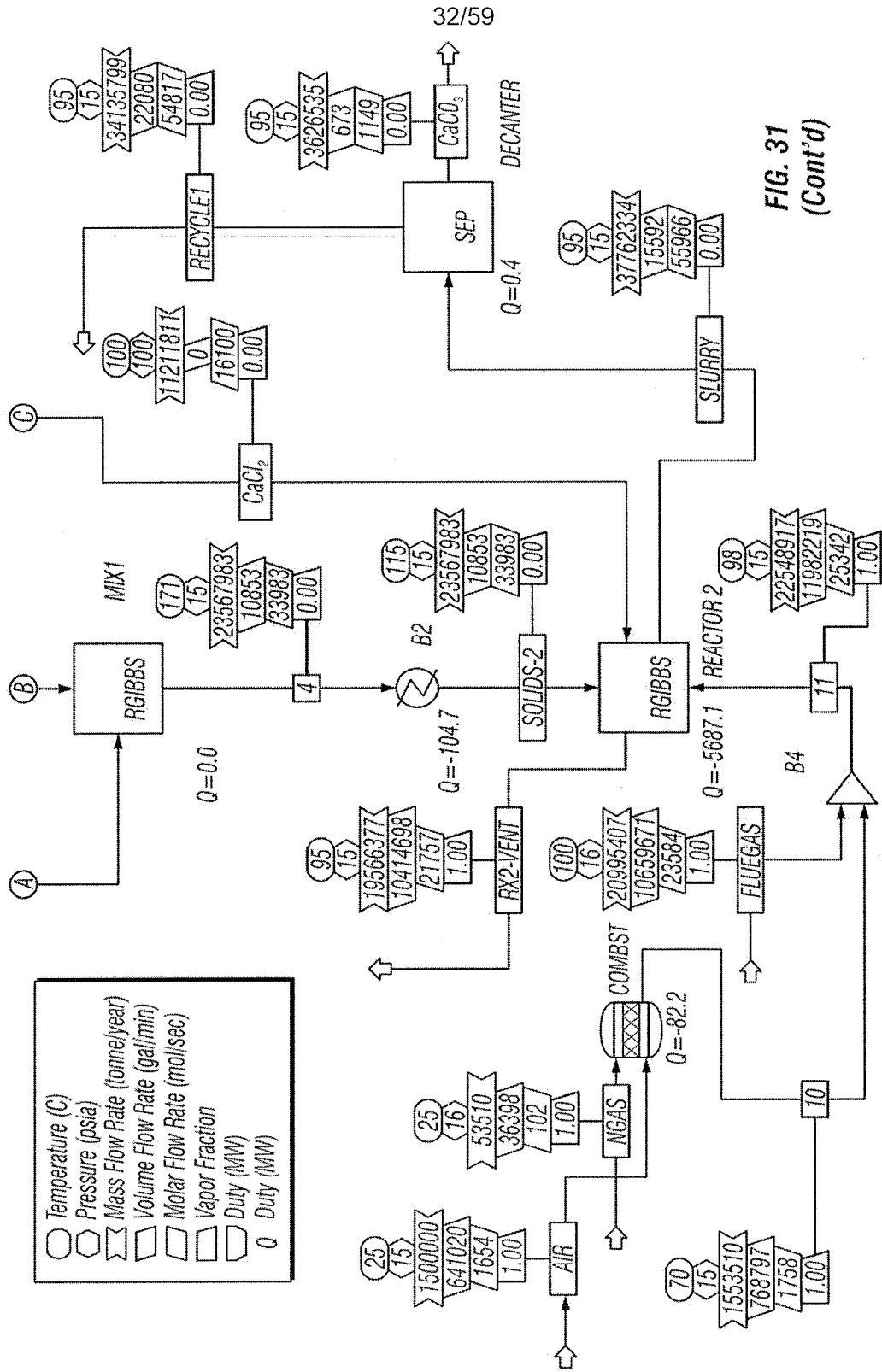
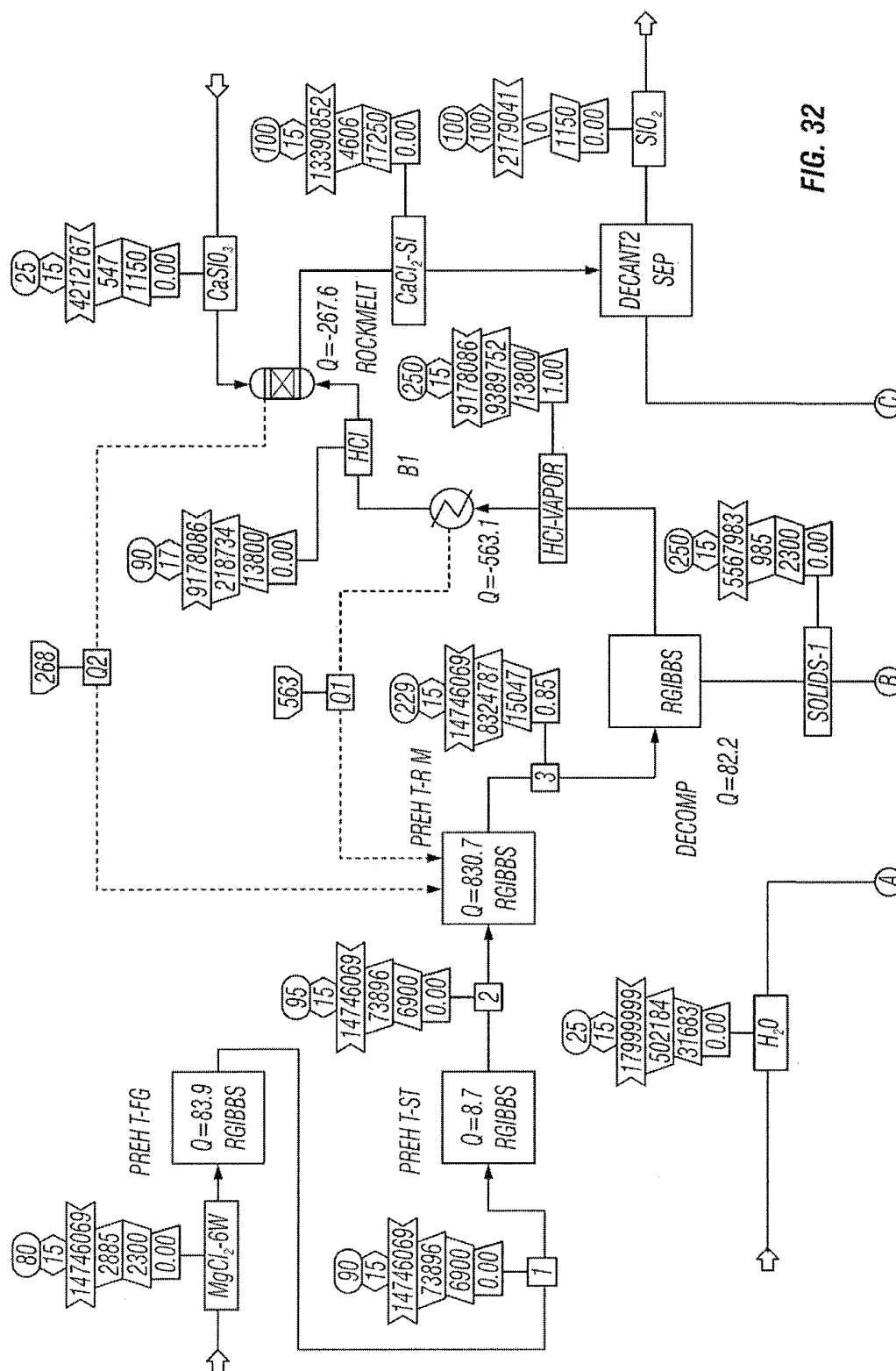


FIG. 31
(Cont'd)



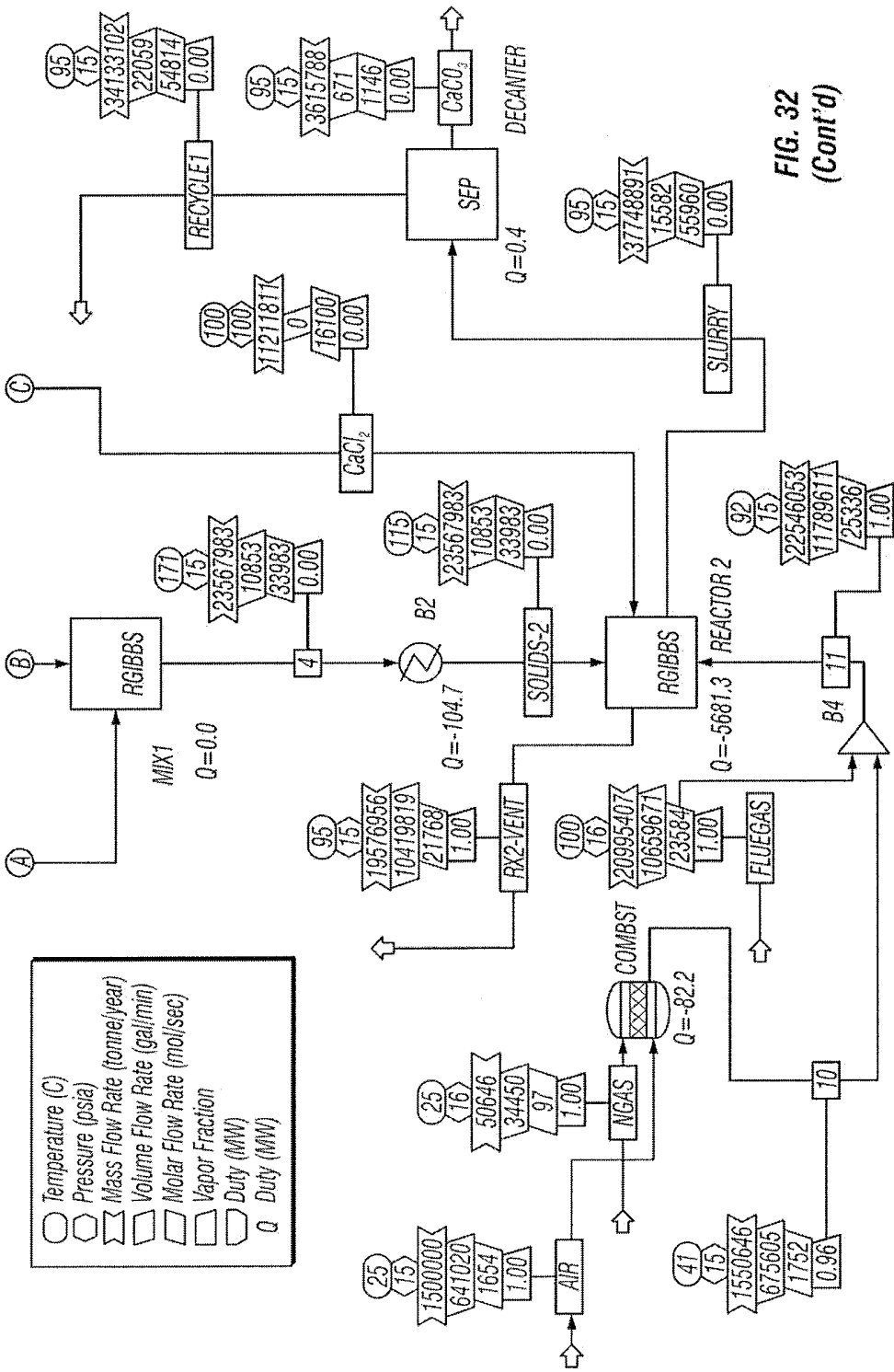


FIG. 32
(Cont'd)

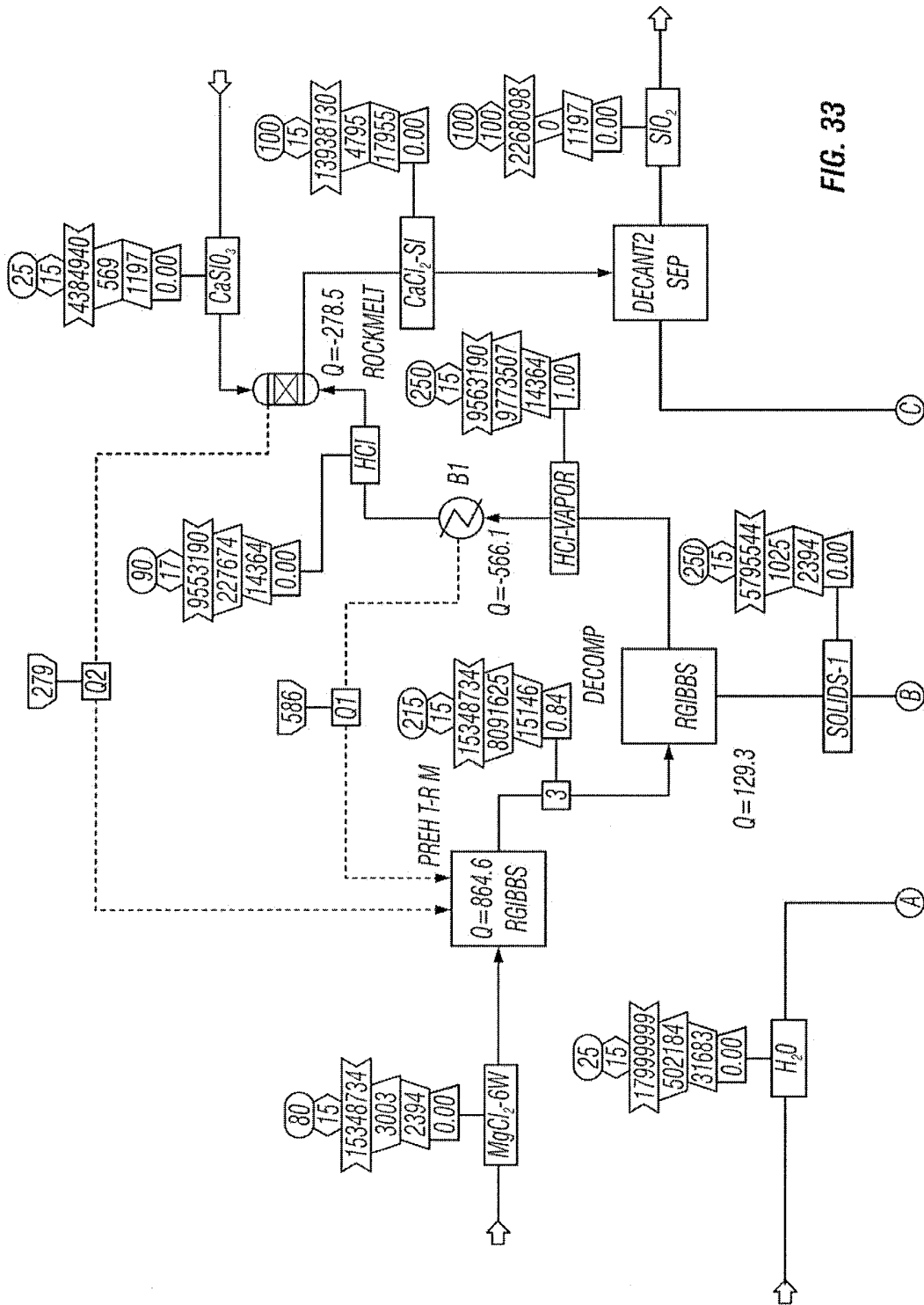


FIG. 33

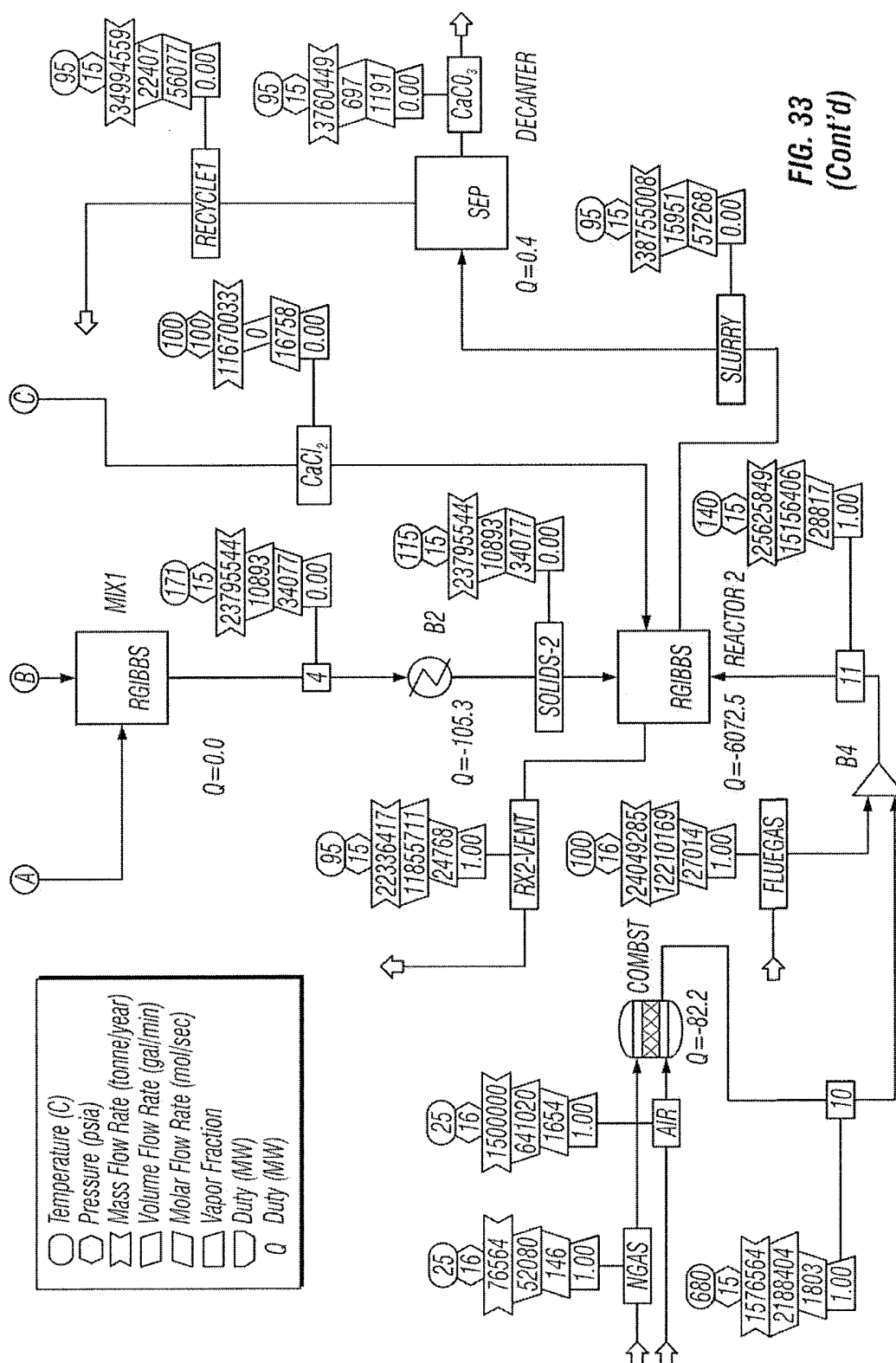


FIG. 33
(Cont'd)

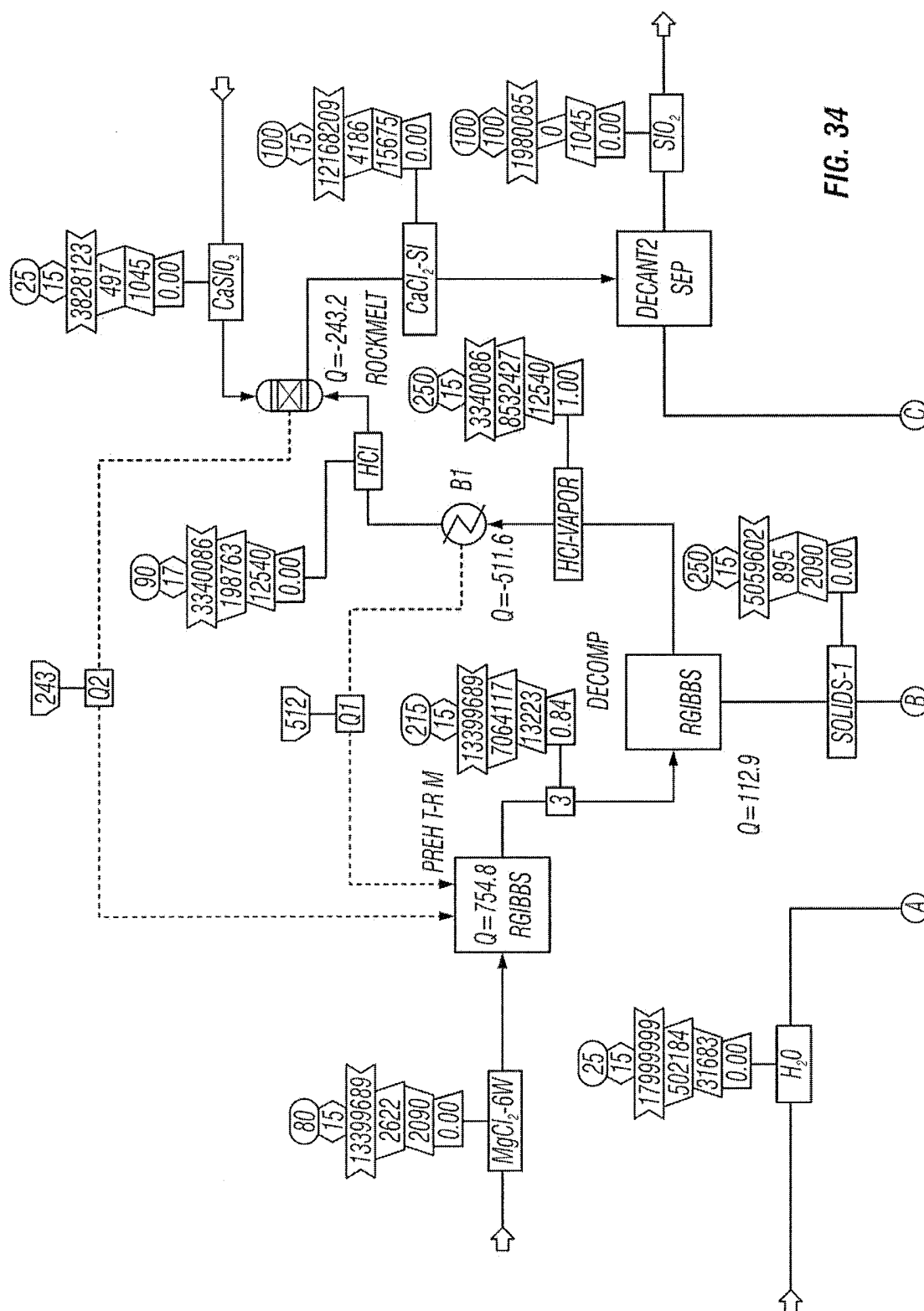
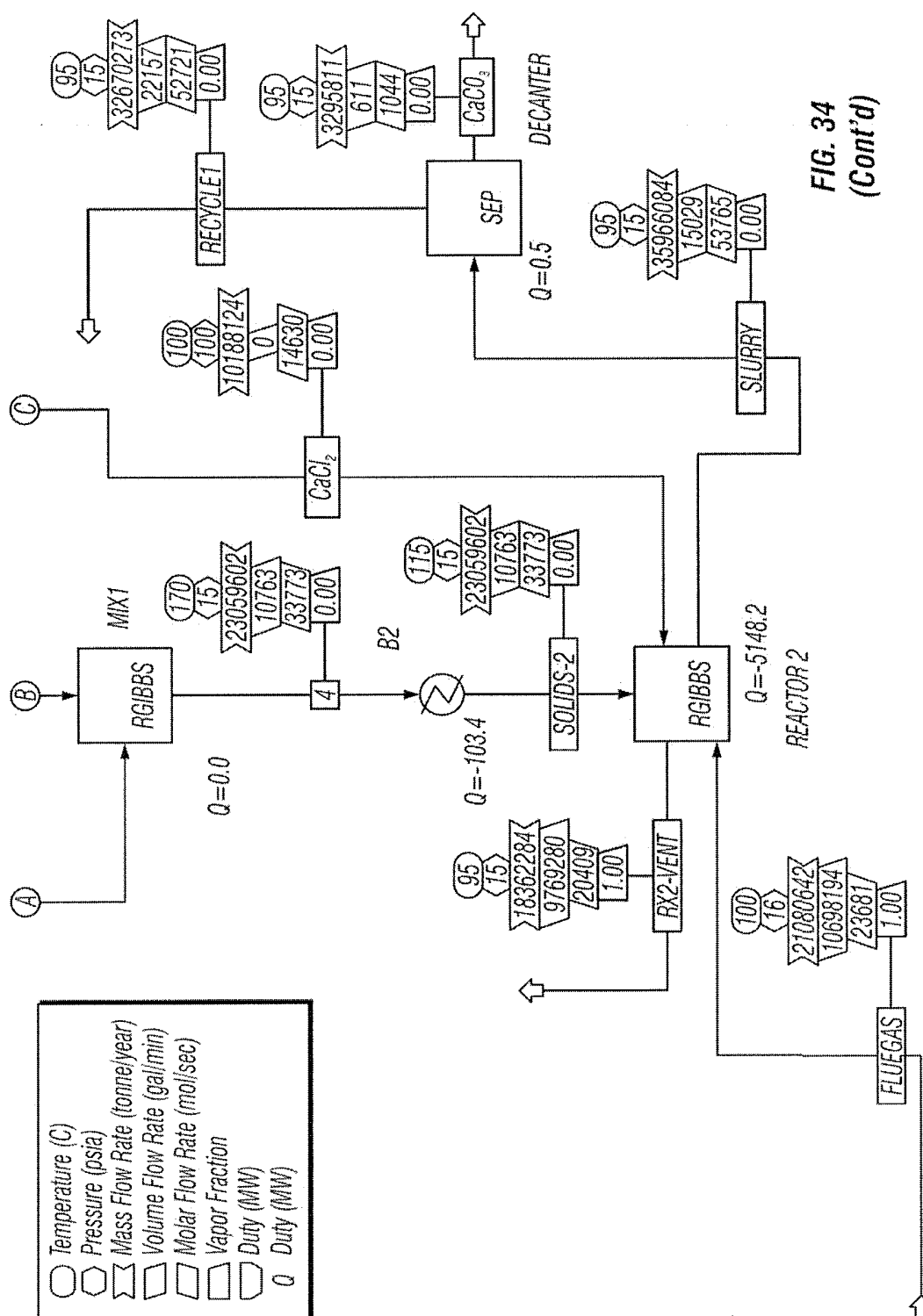


FIG. 34



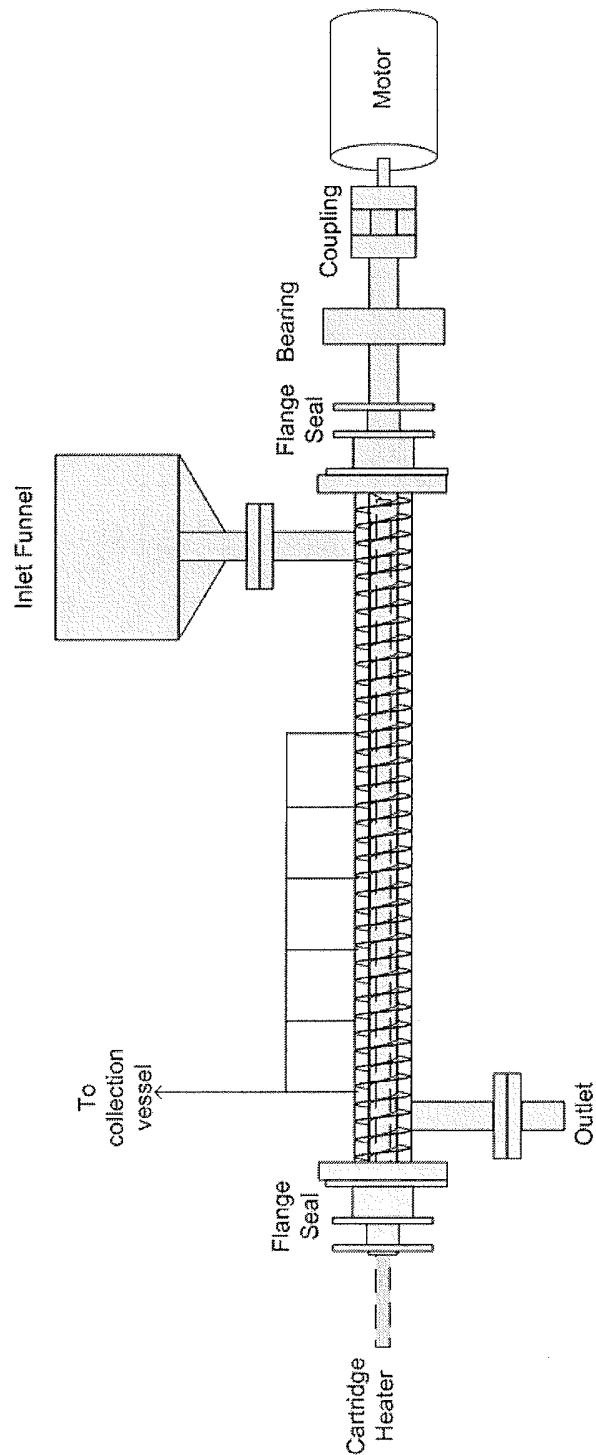


FIG. 35

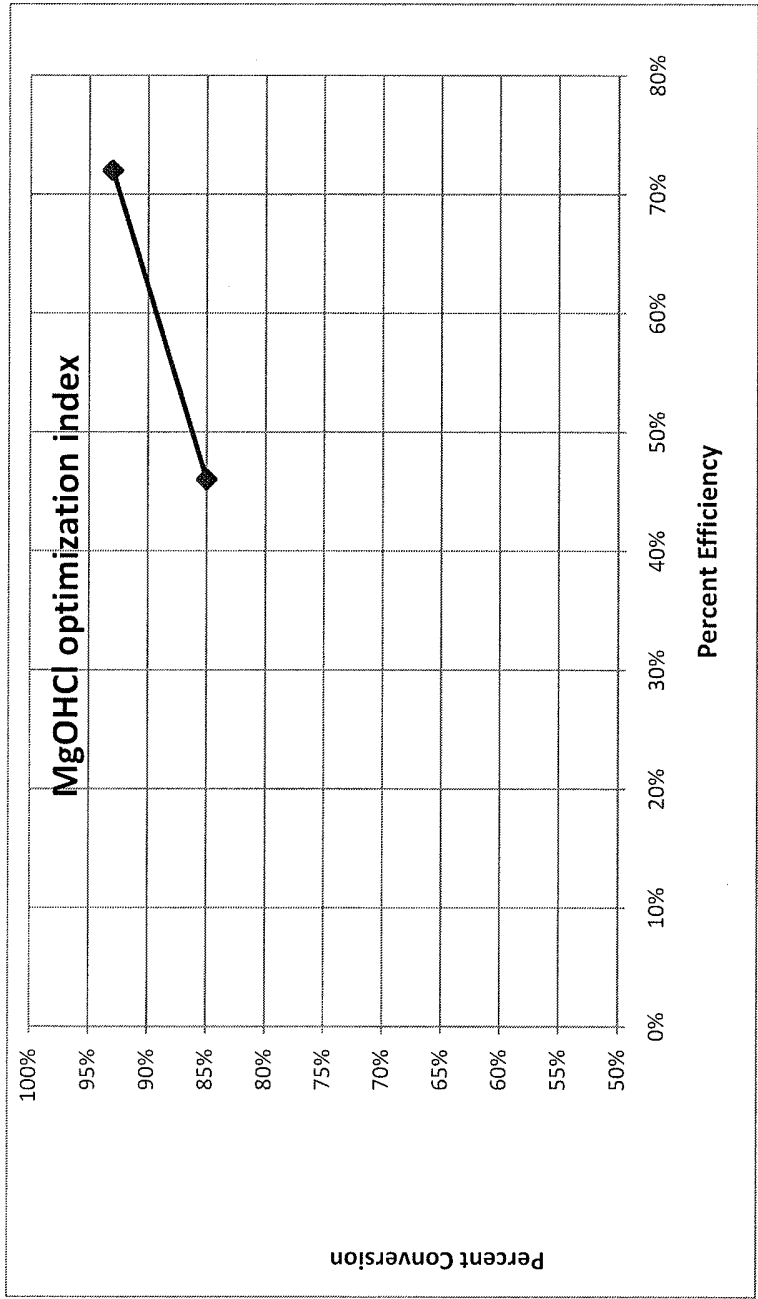


FIG. 36

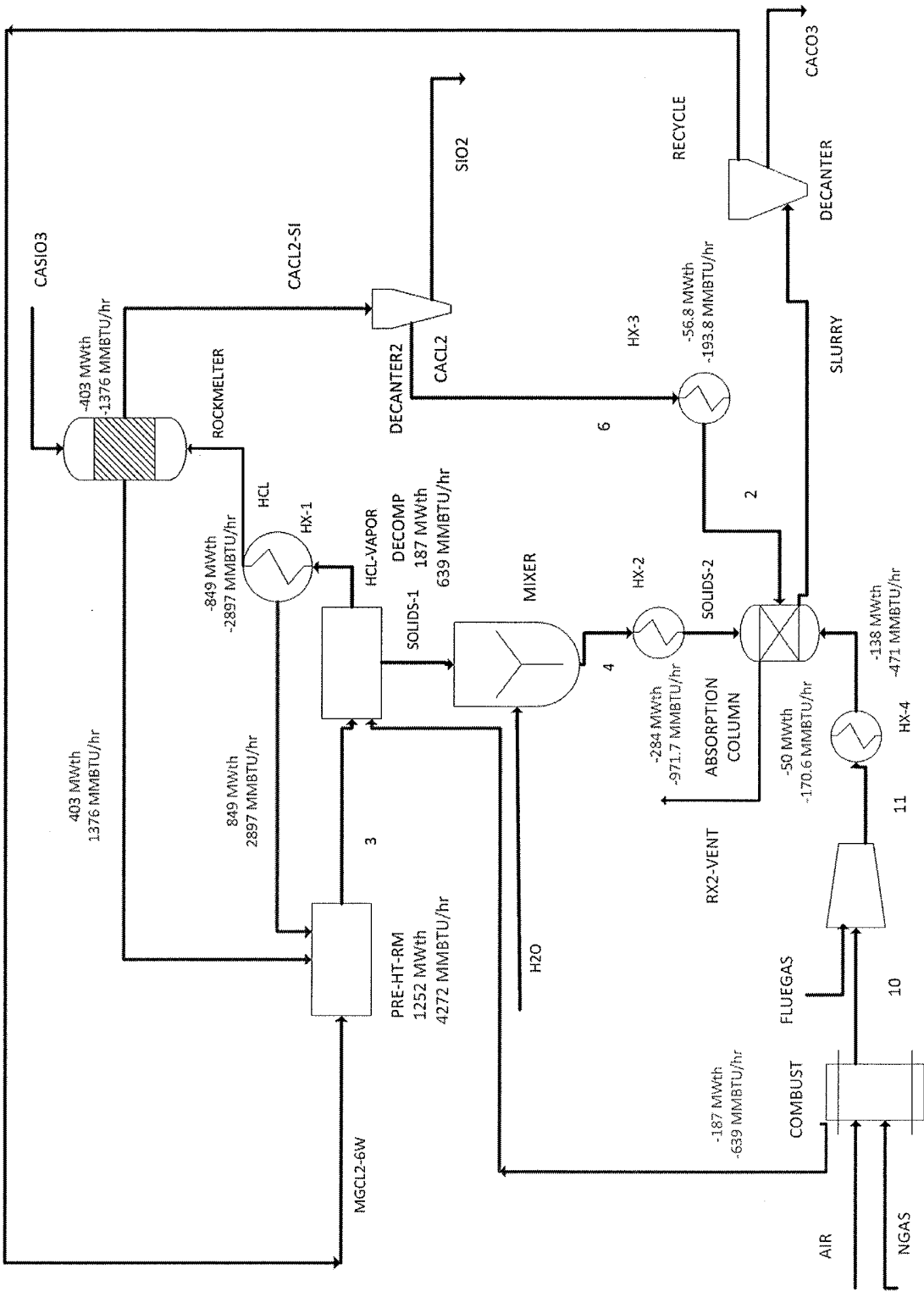
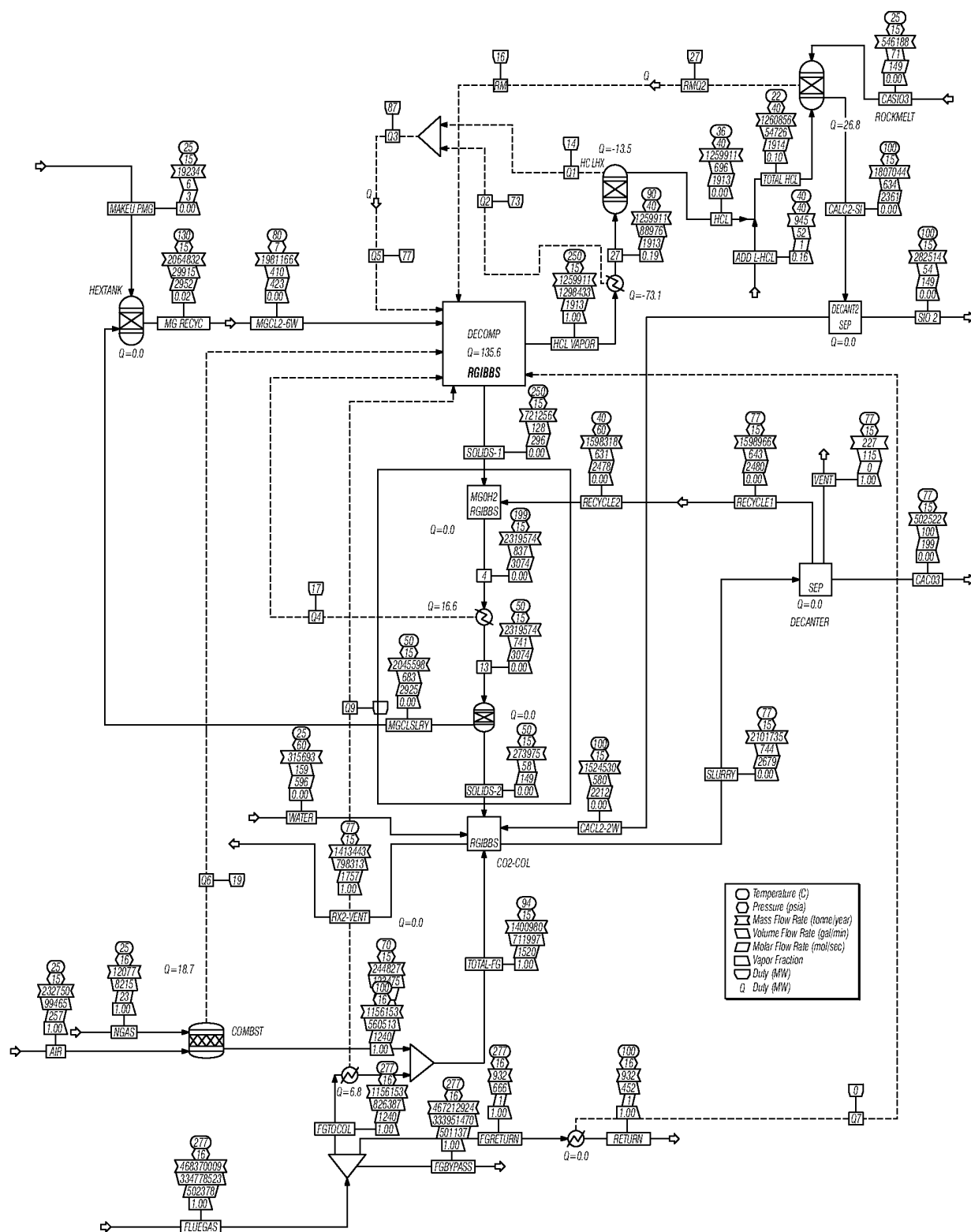


FIG. 37



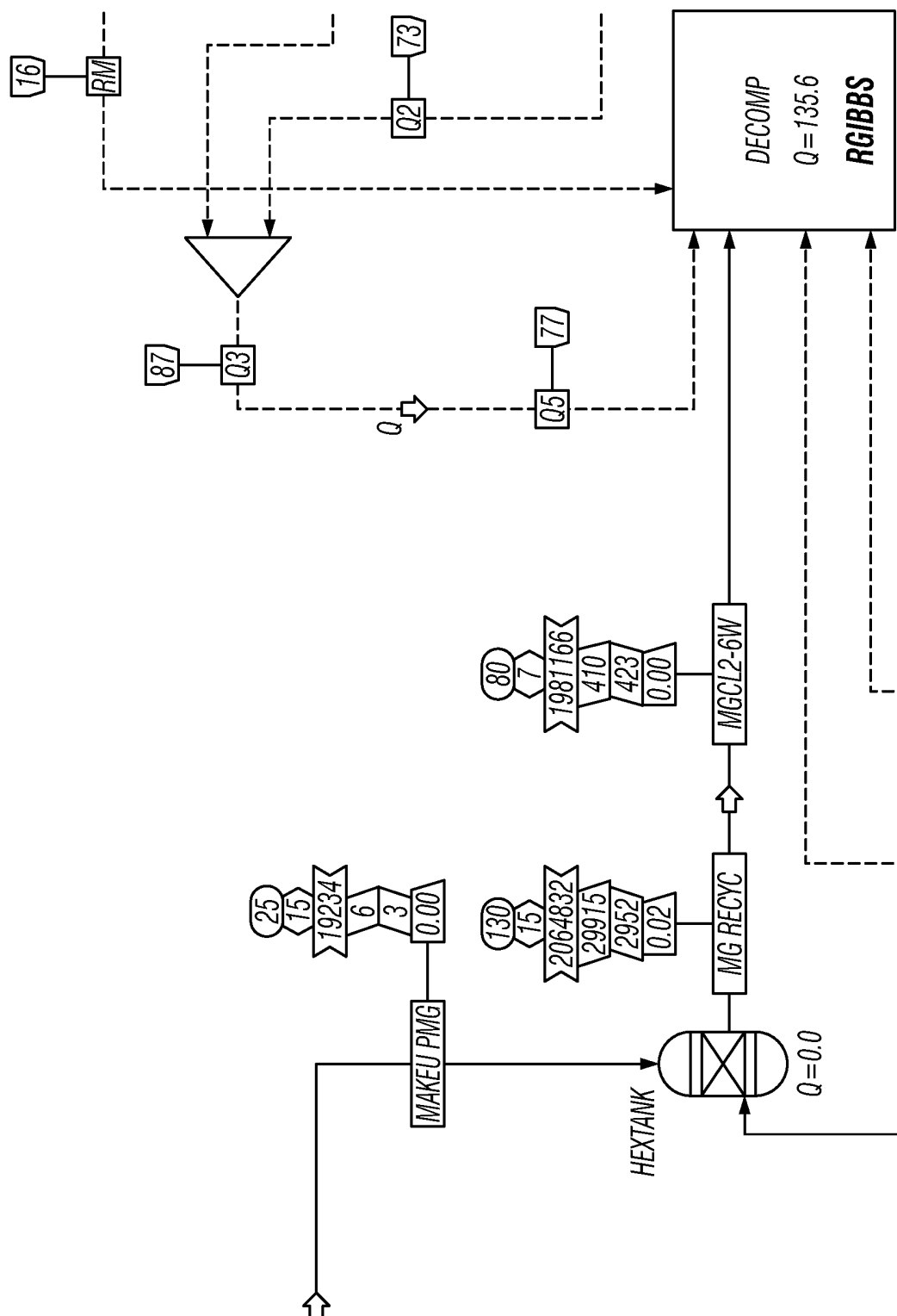


FIG. 38B

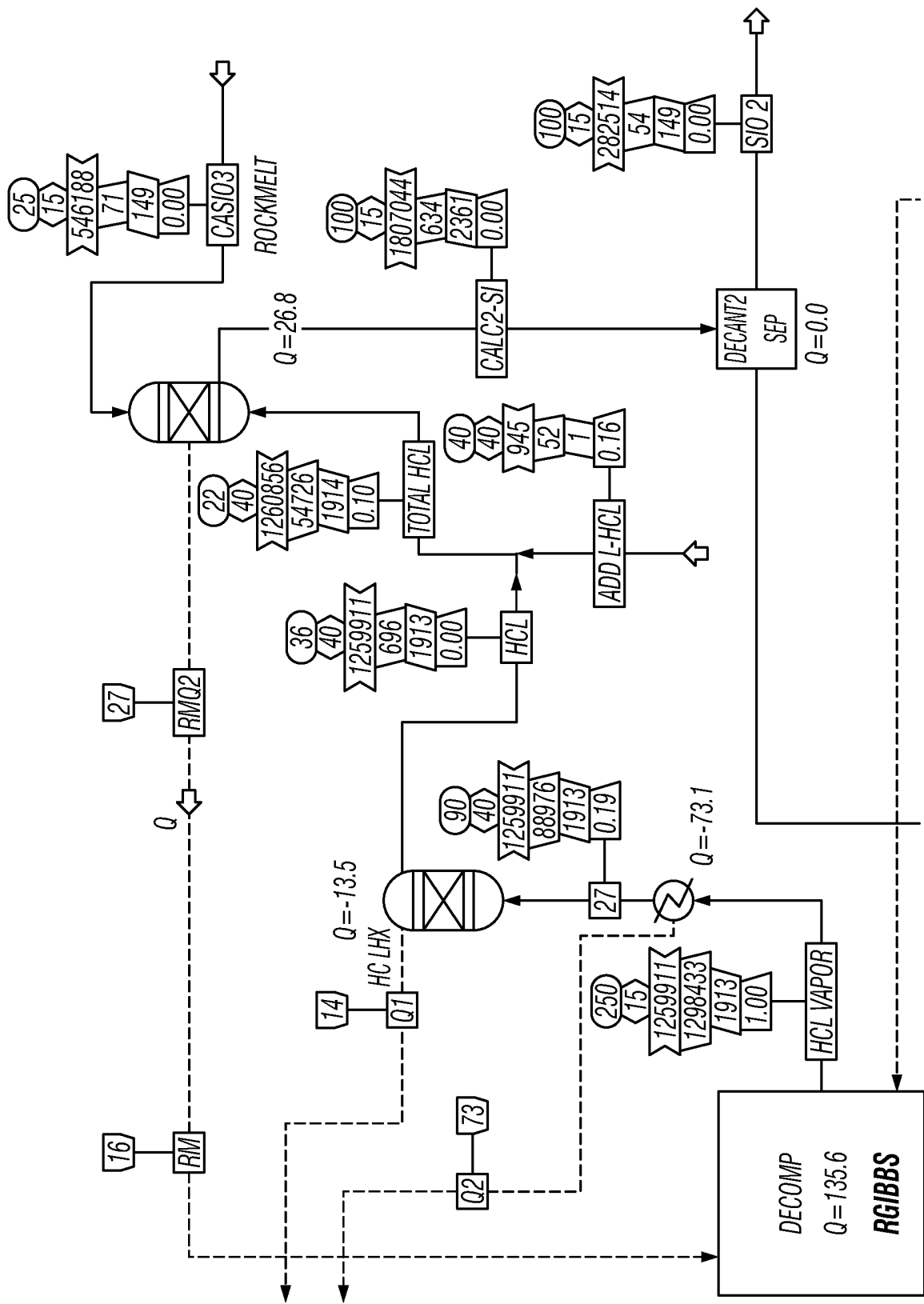


FIG. 38C

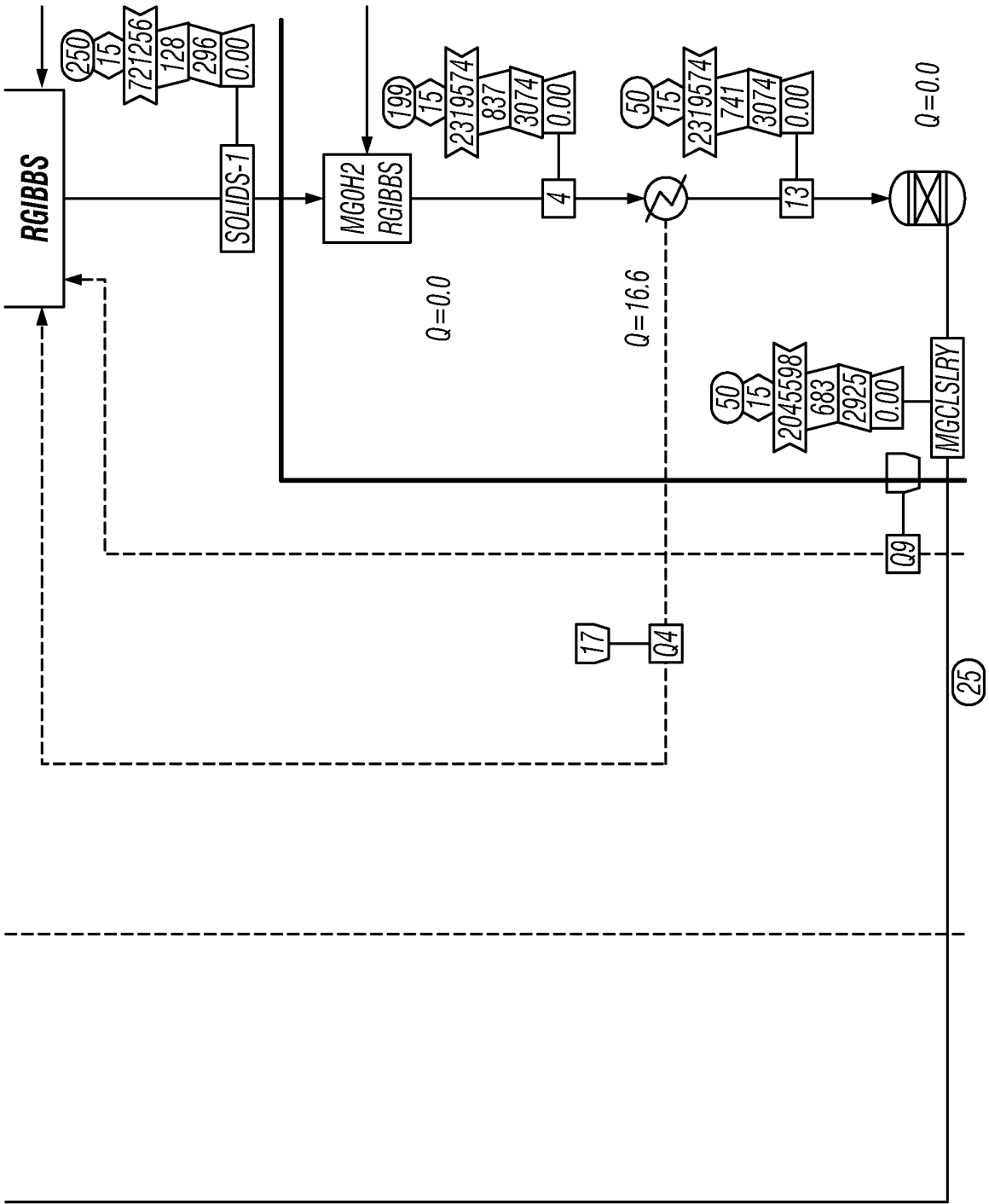


FIG. 38D

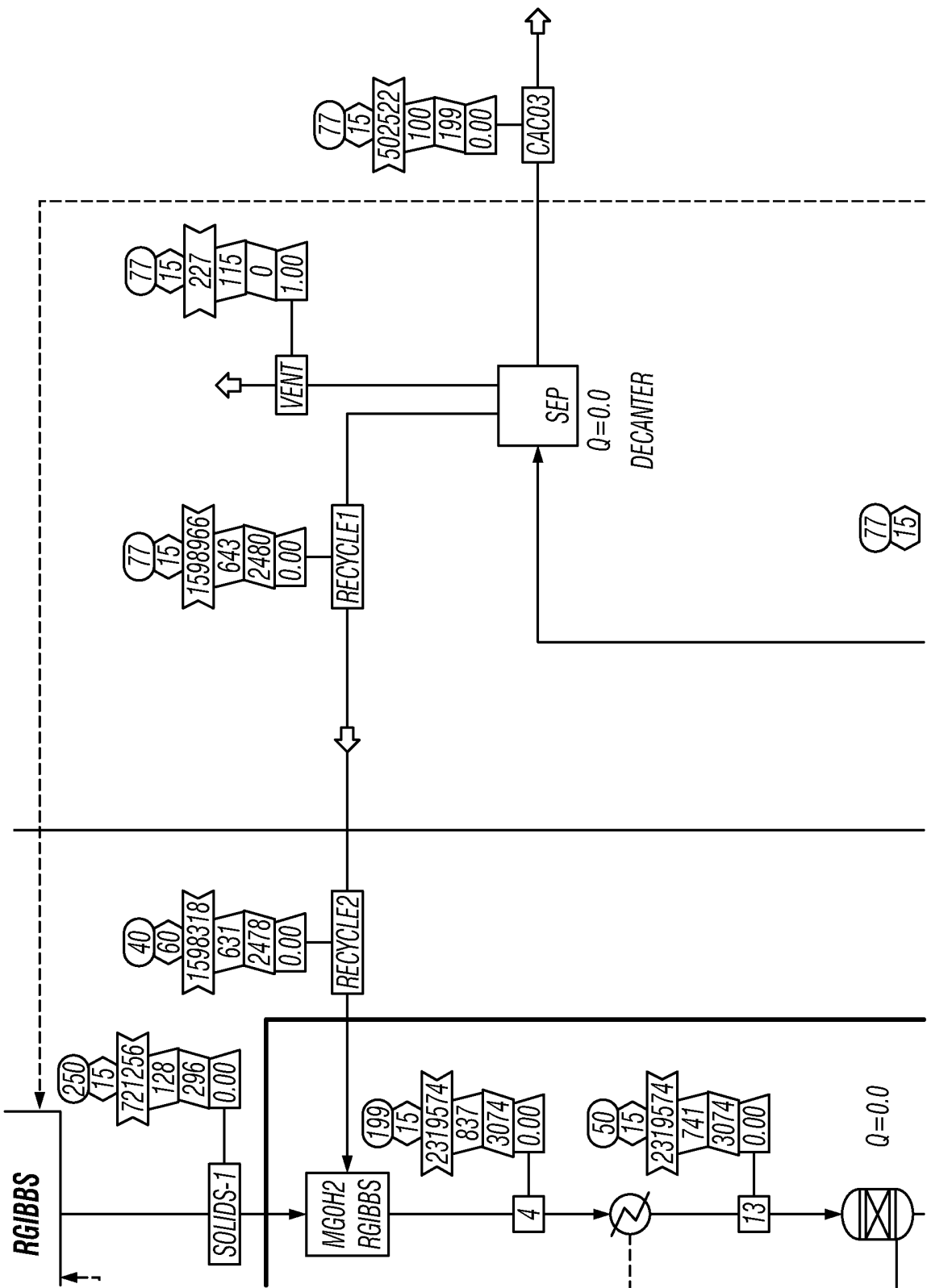


FIG. 38E

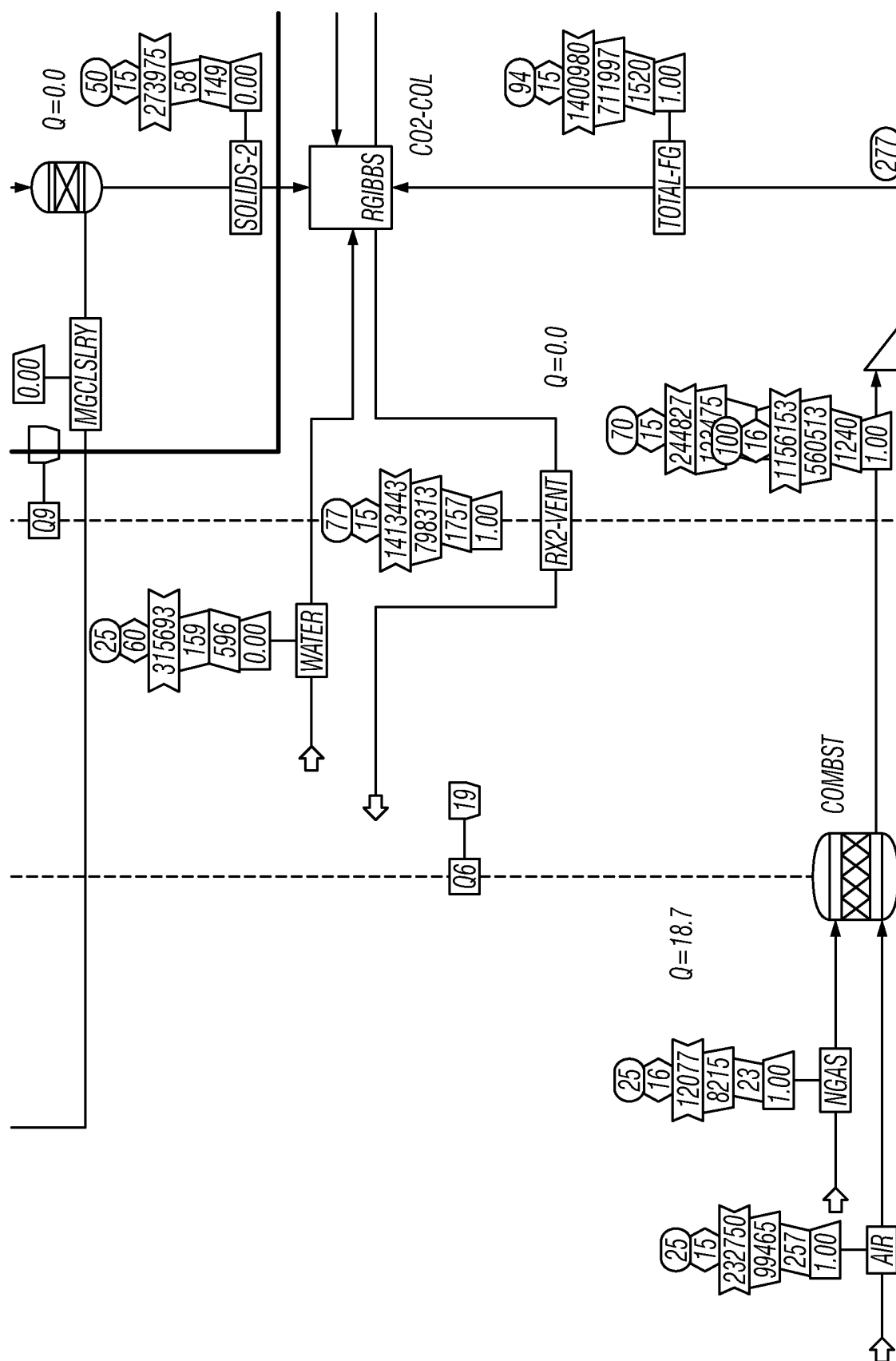


FIG. 38F

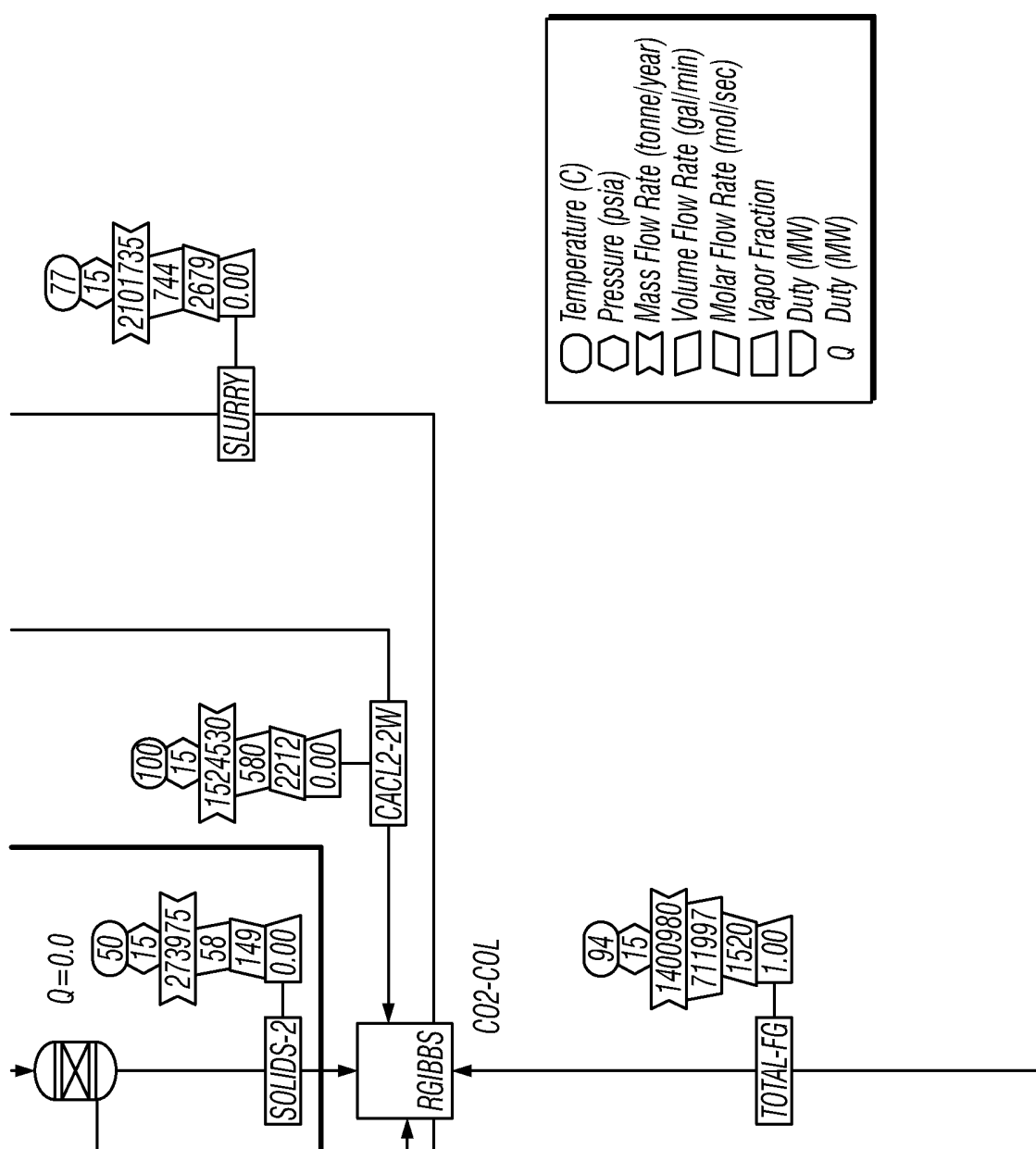


FIG. 38G

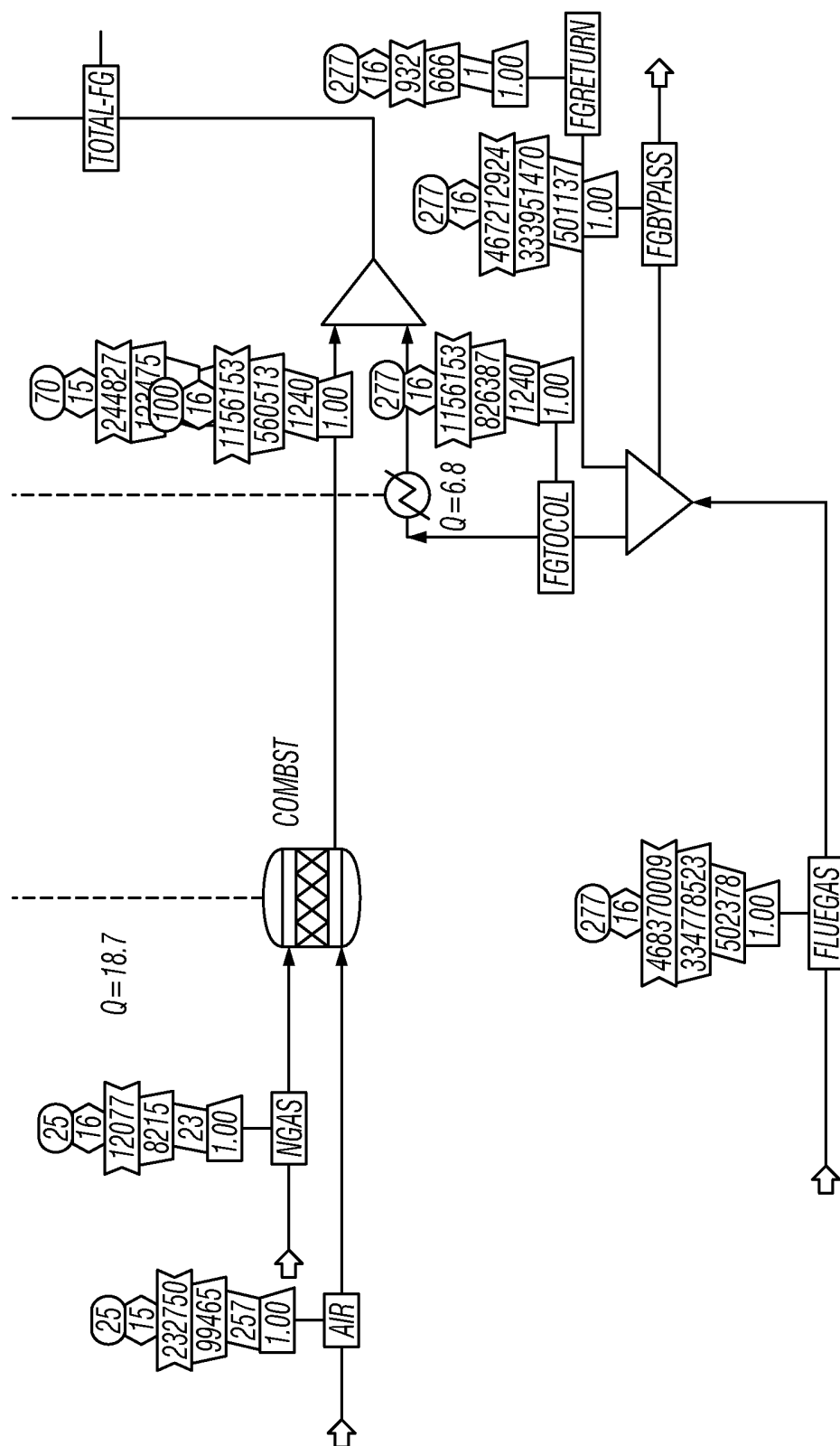


FIG. 38H

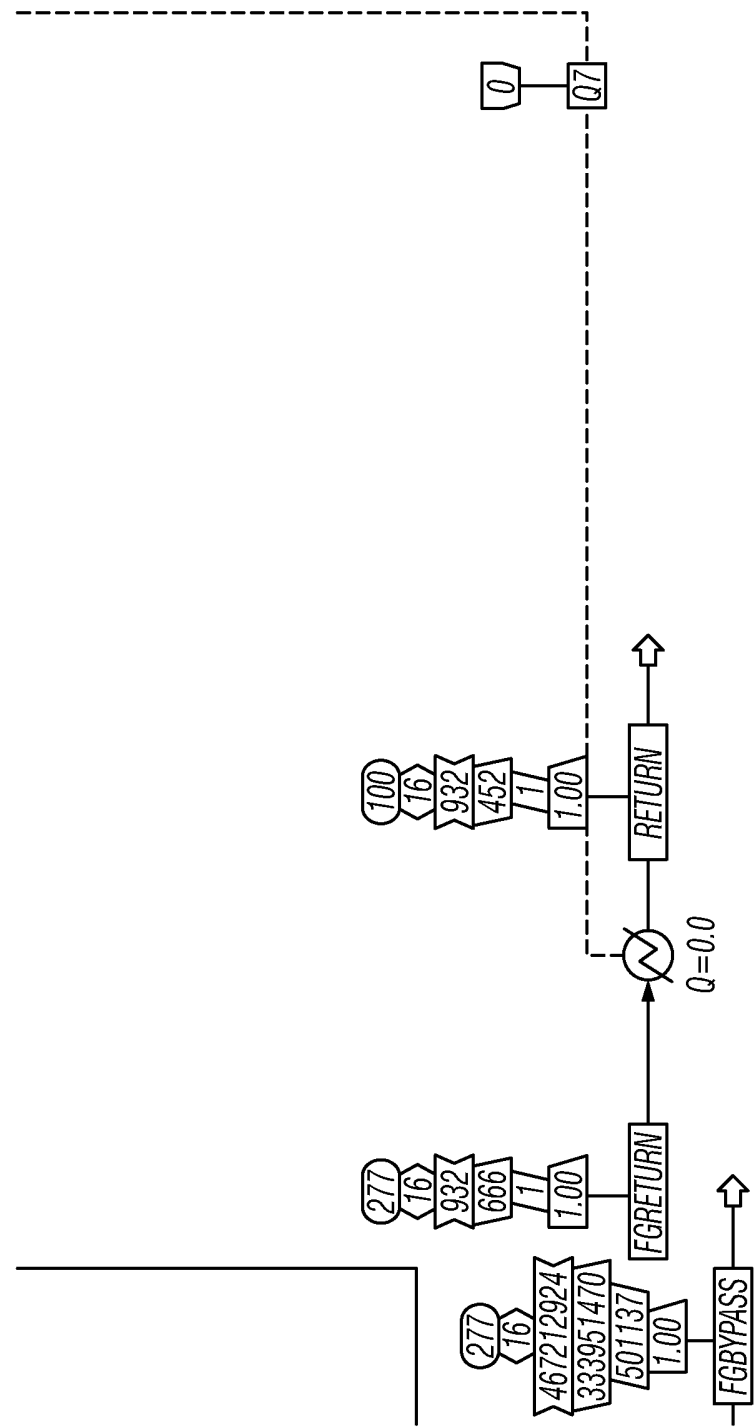


FIG. 38I

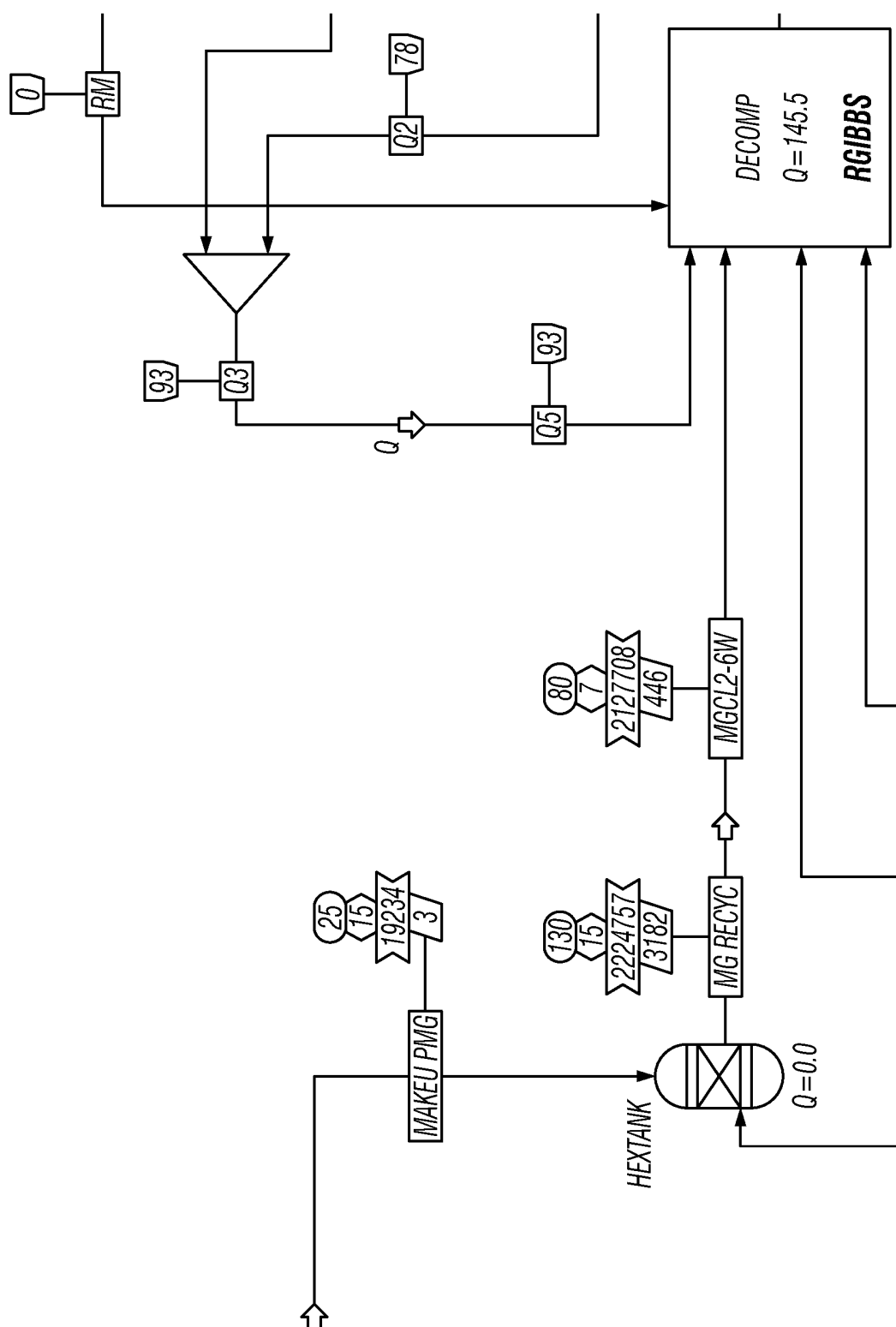


FIG. 39B

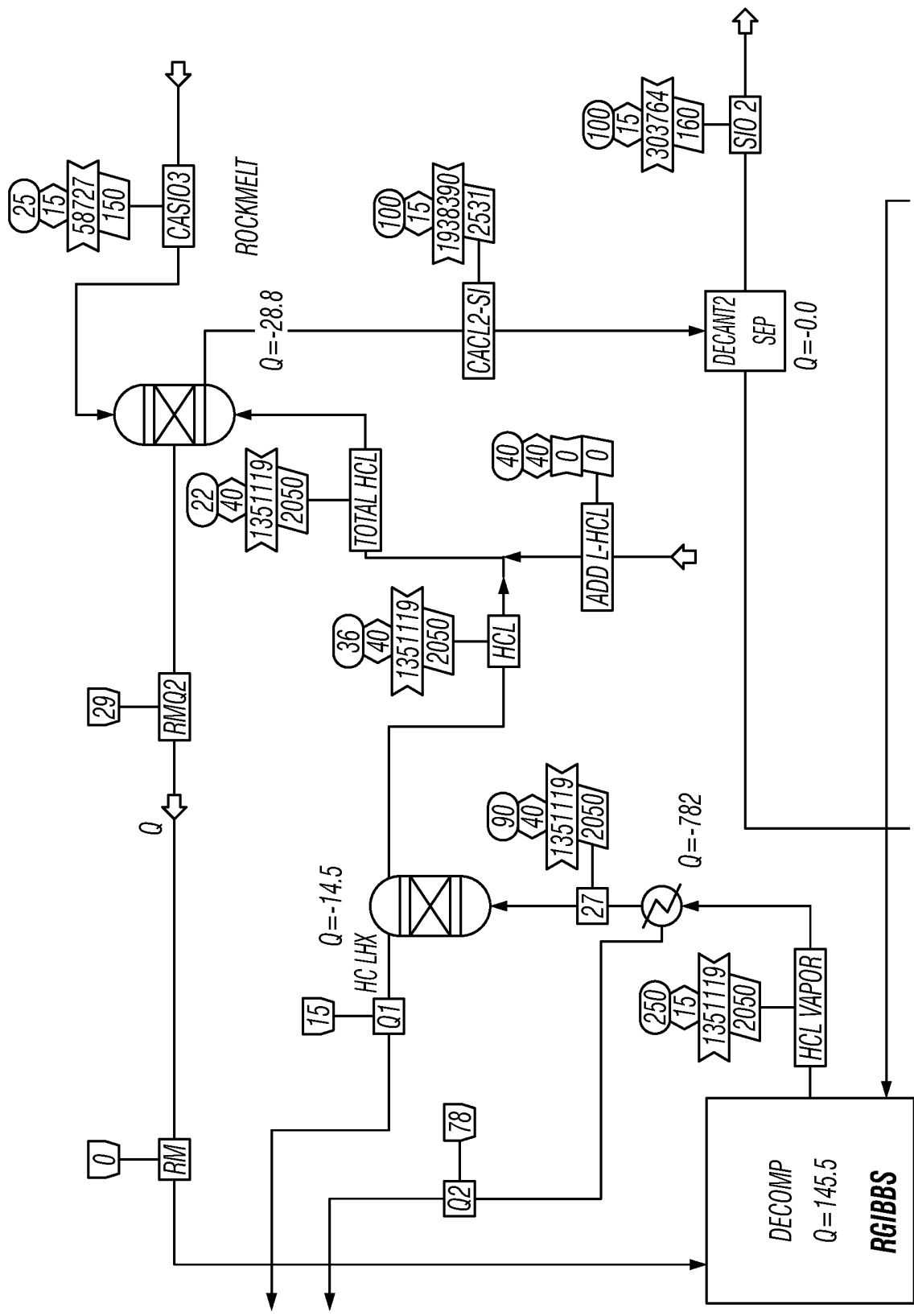


FIG. 39C

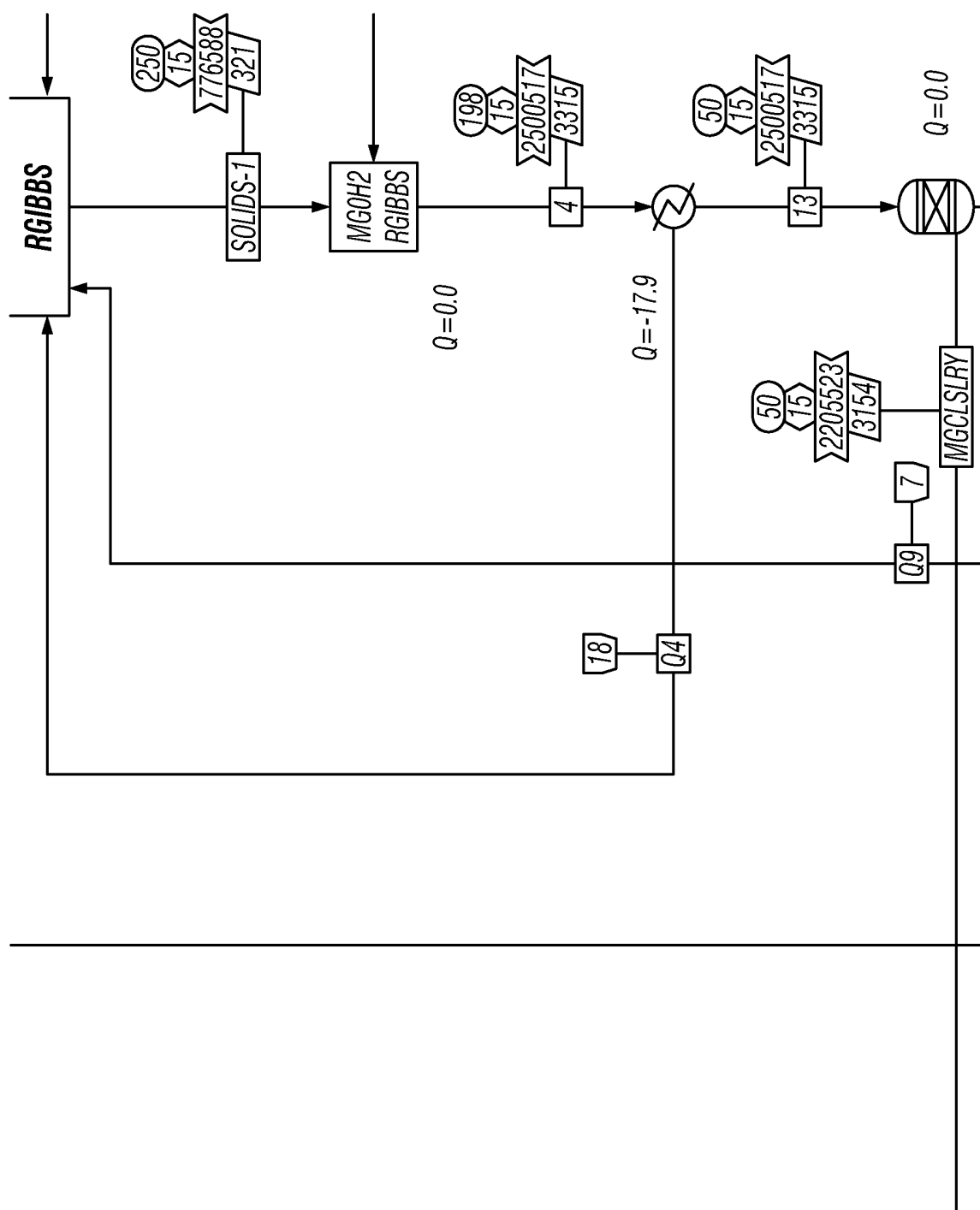


FIG. 39D

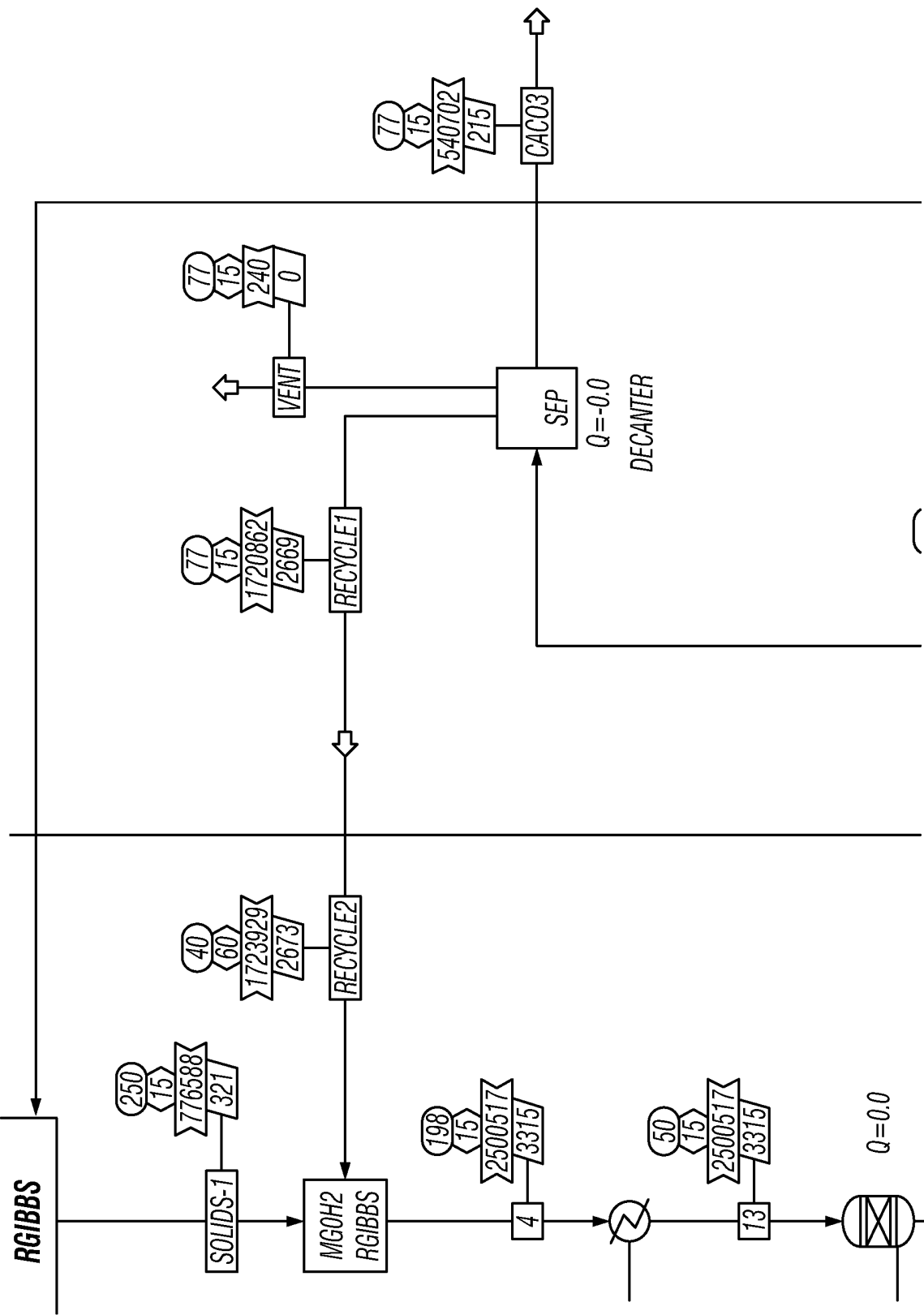


FIG. 39E

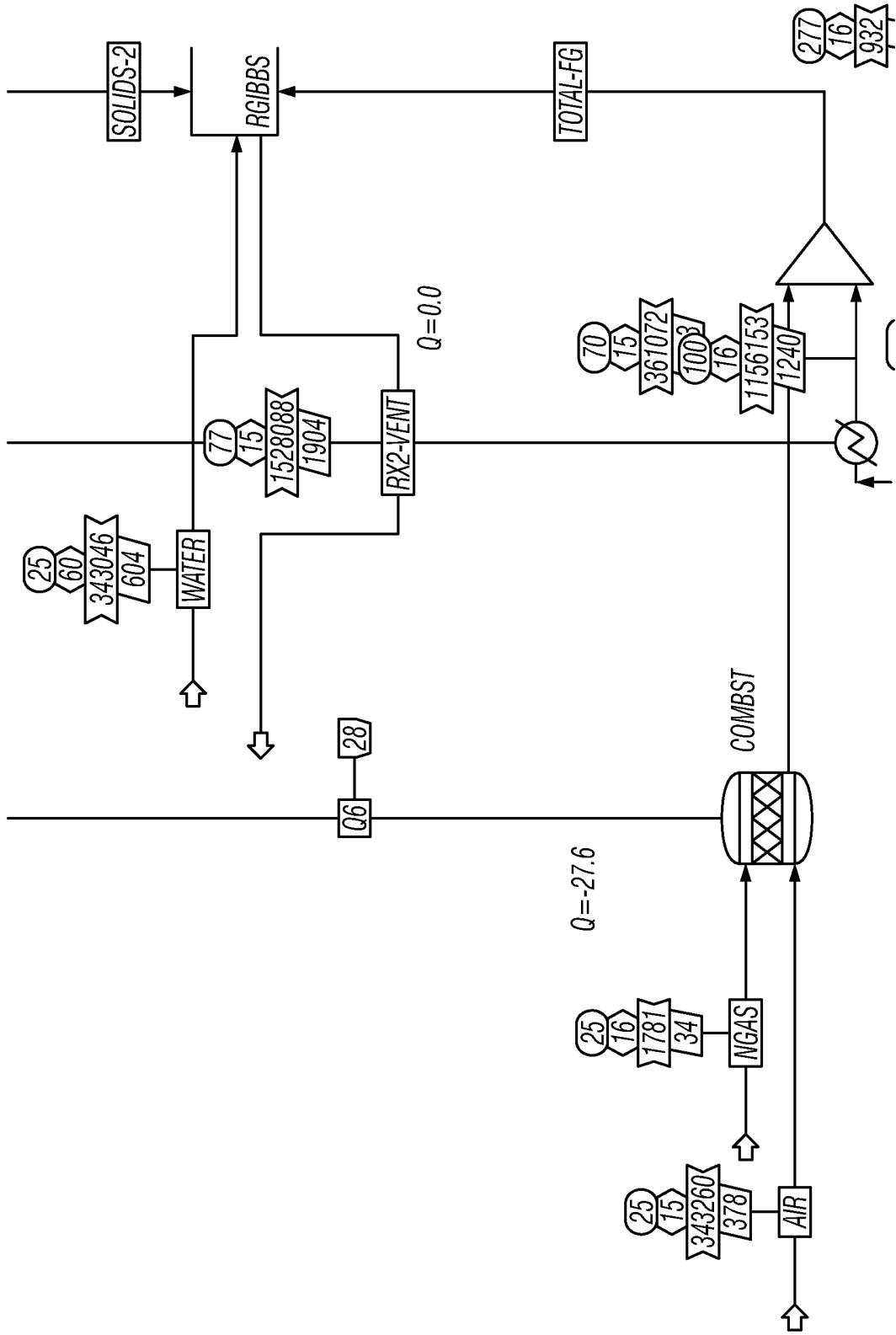


FIG. 39F

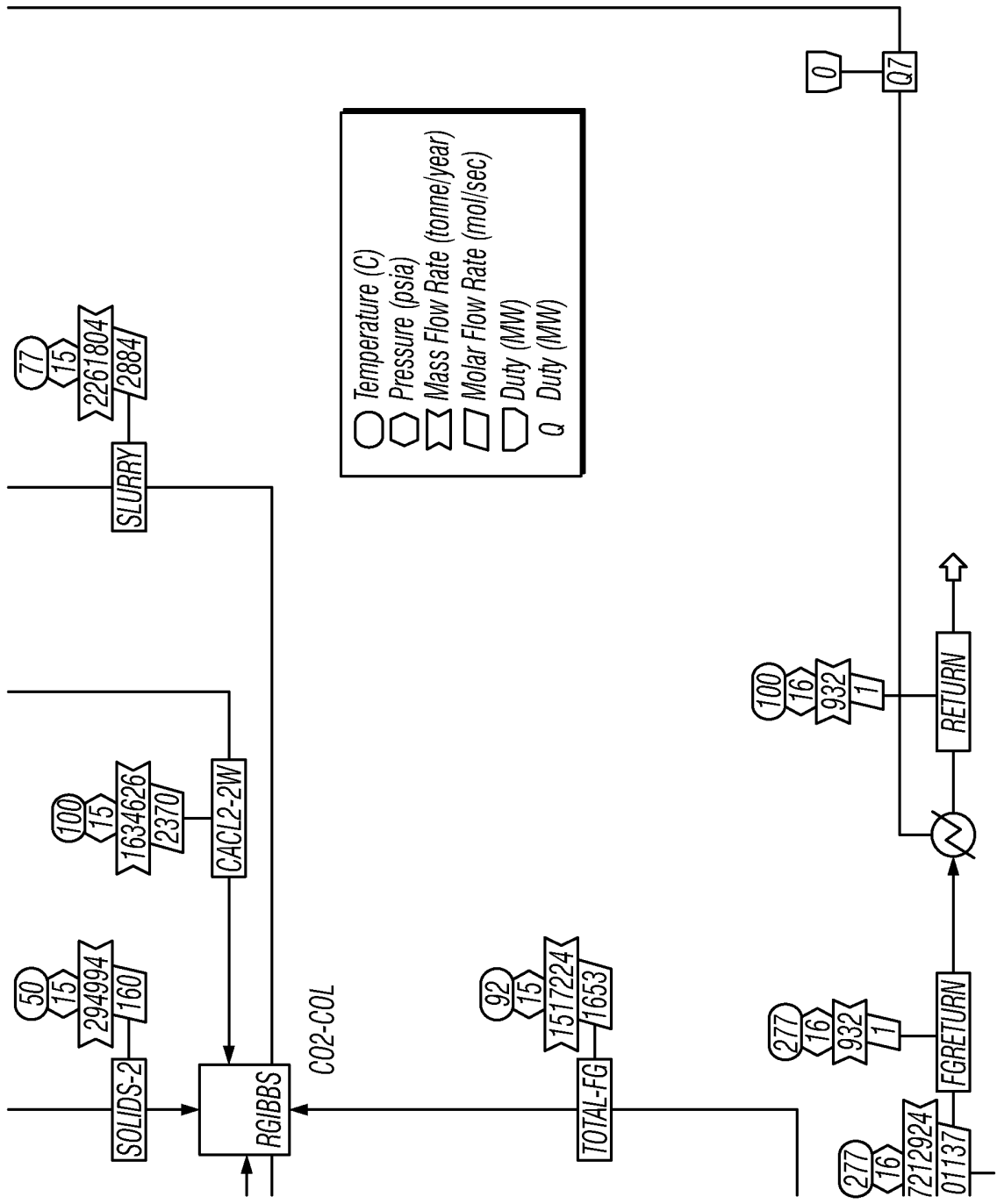


FIG. 39G

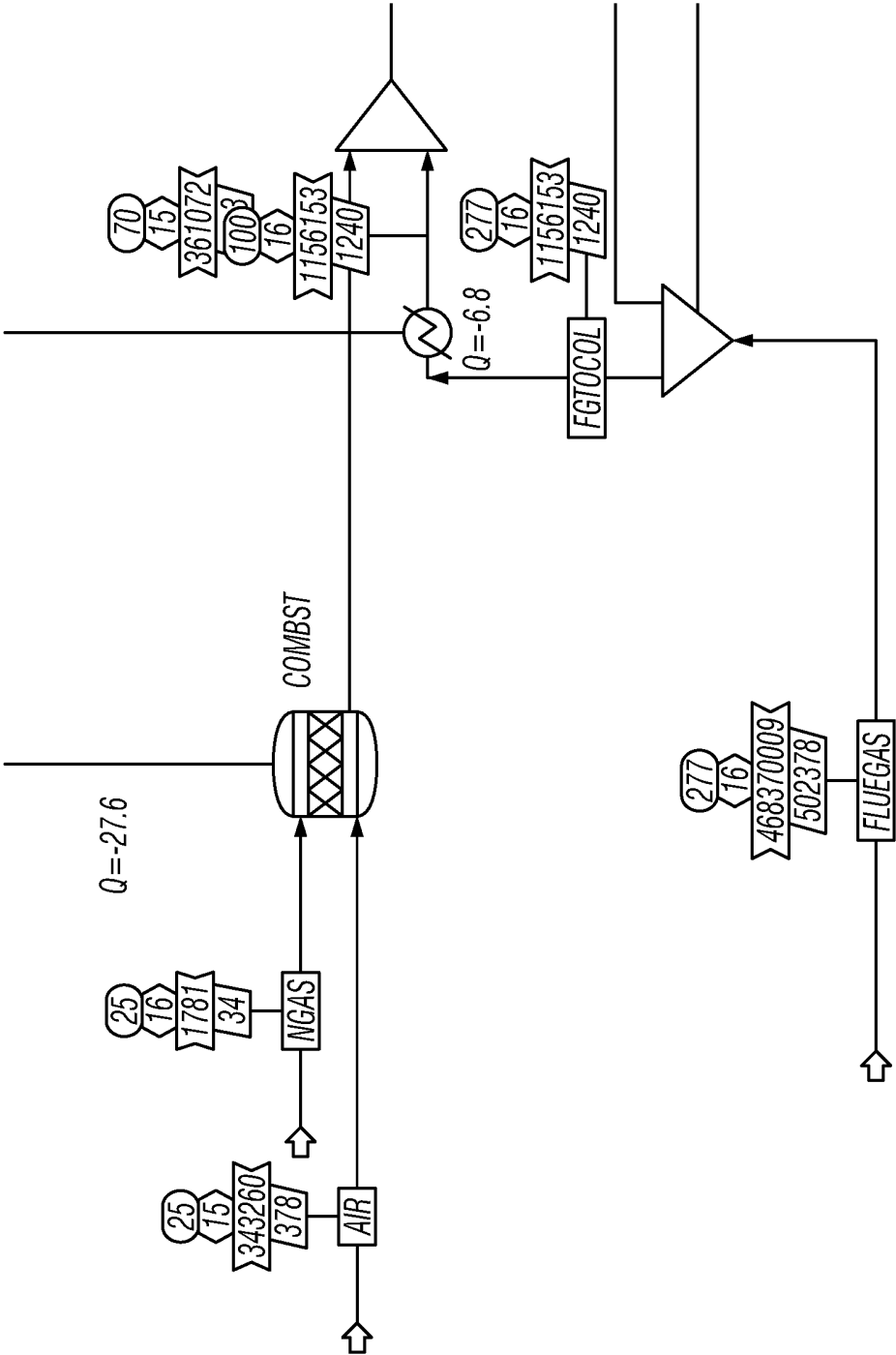


FIG. 39H

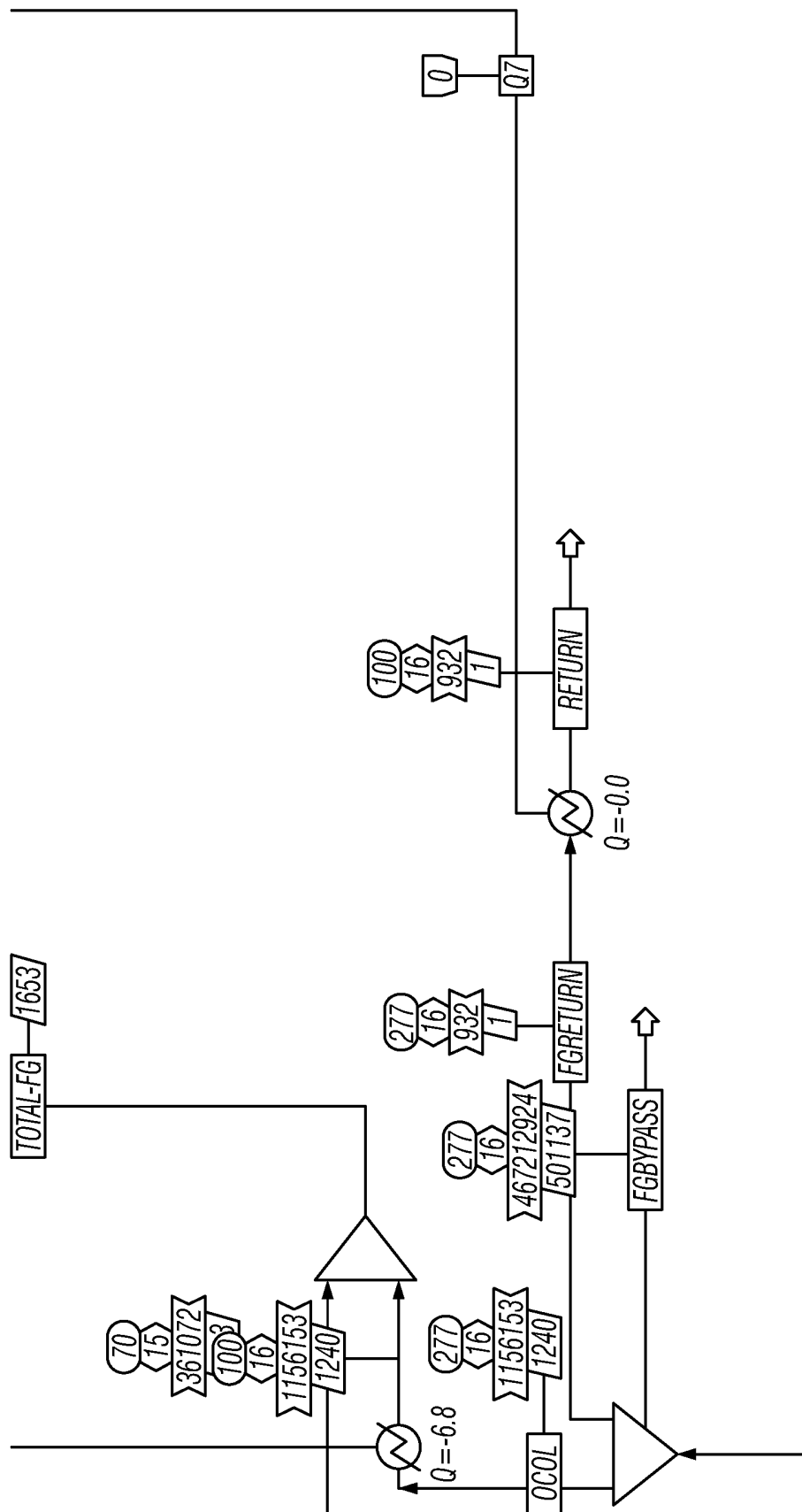


FIG. 39I

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/21264

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/62; C01B 31/24; C01F 11/18 (2013.01)

USPC - 423/220; 423/419.1; 423/431

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - B01D 53/62; C01B 31/24; C01F 11/18 (2013.01)

USPC - 423/220; 423/419.1; 423/431

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 423/220; 423/419.1; 423/431 (See search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

*** Databases: WEST; Patbase; Google

Search Terms Used: Skyonic, carbon dioxide, sequestering, sequestration, Mg(OH)₂, magnesium hydroxide, brucite, MgCl₂, magnesium chloride, Mg(OH)Cl, magnesium hydroxychloride, CaCO₃, calcium carbonate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Haywood et al., "Carbon dioxide sequestration as stable carbonate minerals - environmental barriers," (2001). Environmental Geology, Vol. 41, Is. 1-2 (2001), Pg. 11-16; especially abstract; pg 12, col 2, para 1-2	1-4, 41, 42
Y	US 1,978,403 A (Barstow et al.) 30 October 1934 (30.10.1934), especially pg 1, col 1, ln 66-81	1-4, 41, 42
X,P	US 2012/0034144 A1 (Jones et al.) 09 February 2012 (09.02.2012), entire document	1-4, 41, 42

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

08 March 2013 (08.03.2013)

Date of mailing of the international search report

26 MAR 2013

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/21264

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-40
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.



(12) 发明专利申请

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C01B 31/24 (2006.01)

(22) 申请日 2013.01.11

C01F 11/18 (2006.01)

(30) 优先权数据

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(85) PCT国际申请进入国家阶段日

2014.08.27

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PCT/US2013/021264 2013.01.11

(87) PCT国际申请的公布数据

W02013/106730 EN 2013.07.18

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(54) 发明名称

涉及基于二盐的热解制程的二氧化碳封存

(57) 摘要

本发明涉及节能二氧化碳封存方法,从而使用二盐热解制程将硅酸钙矿物质和CO₂转化成石灰石和沙,所述二盐热解制程允许将热和化学物质自一个步骤循环至另一步骤。在一实施方案中,MgCl₂与水在条件下反应以形成Mg(OH)₂;并且所述Mg(OH)₂产物与CaCl₂和二氧化碳进一步反应以形成MgCl₂、CaCO₃和水。

1. 封存由来源产生的二氧化碳的方法,其包括:

(a) 使 MgCl_2 或其水合物与水于第一掺合物中在适于形成第一产物混合物的条件下反应,所述第一产物混合物包含含有 $\text{Mg}(\text{OH})\text{Cl}$ 的第一步骤 (a) 产物和含有 HCl 的第二步骤 (a) 产物;

(b) 使来自步骤 (a) 的部分或所有所述 $\text{Mg}(\text{OH})\text{Cl}$ 与一定量的水和一定量的 MgCl_2 于第二掺合物中在适于形成第二产物混合物的条件下反应,所述第二产物混合物包含含有 $\text{Mg}(\text{OH})_2$ 的第一步骤 (b) 产物和含有 MgCl_2 的第二步骤 (b) 产物,其中所述水的量足以在所述第二产物混合物中提供大于或等于 6:1 的水与 MgCl_2 的摩尔比;

(c) 使来自所述第一步骤 (b) 产物的部分或所有所述 $\text{Mg}(\text{OH})_2$ 与 CaCl_2 或其水合物和所述来源产生的二氧化碳于第三掺合物中在适于形成第三产物混合物的条件下混合,所述第三产物混合物包含含有 MgCl_2 或其水合物的第一步骤 (c) 产物、含有 CaCO_3 的第二步骤 (c) 产物和含有水的第三步骤 (c) 产物;和

(d) 从所述第三产物混合物分离部分或所有所述 CaCO_3 ,
从而以 CaCO_3 形式封存部分或所有所述二氧化碳。

2. 如权利要求 1 所述的方法,其中步骤 (a) 中的部分或所有所述水以 MgCl_2 水合物形式存在。

3. 如权利要求 1 或 2 所述的方法,其中所述第二产物混合物中水与 MgCl_2 的所述摩尔比介于 6 与 10 之间。

4. 如权利要求 3 所述的方法,其中所述第二产物混合物中水与 MgCl_2 的所述摩尔比介于约 6 与约 7 之间。

5. 如权利要求 1 至 4 中任一项所述的方法,其进一步包括监测所述第二掺合物中 Mg 的浓度。

6. 如权利要求 5 所述的方法,其中基于所述监测来调节第二掺合物中 $\text{Mg}(\text{OH})\text{Cl}$ 的量或水的量。

7. 如权利要求 1 至 6 中任一项所述的方法,其中步骤 (a) 的所述 MgCl_2 是水合 MgCl_2 。

8. 如权利要求 7 所述的方法,其中步骤 (a) 的所述水合 MgCl_2 是 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 。

9. 如权利要求 1 至 8 中任一项所述的方法,其中步骤 (a) 的所述 MgCl_2 中 90 重量%以上是 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 。

10. 如权利要求 1 至 9 中任一项所述的方法,其中所述第一步骤 (a) 产物包含大于 90 重量%的 $\text{Mg}(\text{OH})\text{Cl}$ 。

11. 如权利要求 1 至 10 中任一项所述的方法,其进一步包括分离所述步骤 (b) 产物。

12. 如权利要求 11 所述的方法,其中步骤 (b) 的所述 $\text{Mg}(\text{OH})_2$ 产物是固体且其中分离所述步骤 (b) 产物包括使部分或所有所述固体 $\text{Mg}(\text{OH})_2$ 与所述水和所述 MgCl_2 分离。

13. 如权利要求 1 至 12 中任一项所述的方法,其中步骤 (b) 的所述 MgCl_2 产物是 MgCl_2 水溶液。

14. 如权利要求 1 至 13 中任一项所述的方法,其中在步骤 (b) 或步骤 (c) 中形成的部分或所有所述 MgCl_2 是在步骤 (a) 中使用的所述 MgCl_2 。

15. 如权利要求 1 至 13 中任一项所述的方法,其中步骤 (a) 中的部分或所有所述水是以蒸汽或超临界水的形式存在。

16. 如权利要求 1 至 15 中任一项所述的方法,其中步骤 (a) 的部分或所有所述水是从步骤 (c) 的所述水获得的。

17. 如权利要求 1 至 16 中任一项所述的方法,其进一步包括:

(e) 在适于形成第三产物混合物的条件下混合硅酸钙矿物质与 HCl,所述第三产物混合物包含 CaCl_2 、水和二氧化硅。

18. 如权利要求 17 所述的方法,其中步骤 (e) 中的部分或所有所述 HCl 是从步骤 (a) 获得的。

19. 如权利要求 17 所述的方法,其中步骤 (e) 进一步包括将所述硅酸钙矿物质与 HCl 一起搅动。

20. 如权利要求 17 至 19 中任一项所述的方法,其中回收在步骤 (e) 中生成的部分或所有热。

21. 如权利要求 17 至 20 中任一项所述的方法,其中步骤 (c) 的部分或所有所述 CaCl_2 是步骤 (e) 的所述 CaCl_2 。

22. 如权利要求 17 至 21 中任一项所述的方法,其进一步包括分离步骤,其中从在步骤 (e) 中形成的所述 CaCl_2 去除所述二氧化硅。

23. 如权利要求 17 至 22 中任一项所述的方法,其中步骤 (a) 的部分或所有所述水是从步骤 (e) 的所述水获得的。

24. 如权利要求 17 至 22 中任一项所述的方法,其中步骤 (e) 的所述硅酸钙矿物质包括链状硅酸钙。

25. 如权利要求 17 至 22 中任一项所述的方法,其中步骤 (e) 的所述硅酸钙矿物质包括 CaSiO_3 。

26. 如权利要求 17 至 22 中任一项所述的方法,其中步骤 (e) 的所述硅酸钙矿物质包括透辉石 ($\text{CaMg}[\text{Si}_2\text{O}_6]$) 或透闪石 $\text{Ca}_2\text{Mg}_5\{[\text{OH}]\text{Si}_4\text{O}_{11}\}_2$ 。

27. 如权利要求 17 至 22 中任一项所述的方法,其中所述硅酸钙进一步包括铁硅酸盐和/或锰硅酸盐。

28. 如权利要求 27 所述的方法,其中所述铁硅酸盐是铁橄榄石 ($\text{Fe}_2[\text{SiO}_4]$)。

29. 如权利要求 1 至 28 中任一项所述的方法,其中所述二氧化碳呈烟道气形式,其中所述烟道气进一步包含 N_2 和 H_2O 。

30. 如权利要求 1 至 29 中任一项所述的方法,其中步骤 (a) 的适宜反应条件包括约 200°C 至约 500°C 的温度。

31. 如权利要求 30 所述的方法,其中所述温度为约 230°C 至约 260°C。

32. 如权利要求 30 所述的方法,其中所述温度为约 250°C。

33. 如权利要求 30 所述的方法,其中所述温度为约 200°C 至约 250°C。

34. 如权利要求 30 所述的方法,其中所述温度为约 240°C。

35. 如权利要求 1 至 34 中任一项所述的方法,其中步骤 (b) 的适宜反应条件包括约 140°C 至约 240°C 的温度。

36. 如权利要求 1 至 35 中任一项所述的方法,其中步骤 (c) 的适宜反应条件包括约 20°C 至约 100°C 的温度。

37. 如权利要求 36 所述的方法,其中所述温度为约 25°C 至约 95°C。

38. 如权利要求 17 至 37 中任一项所述的方法,其中步骤 (e) 的适宜反应条件包括约 50℃至约 200℃的温度。

39. 如权利要求 38 所述的方法,其中所述温度为约 90℃至约 150℃。

40. 如权利要求 1 至 39 中任一项所述的方法,其中将步骤 (a) 的部分或所有所述氯化氢与水混合以形成盐酸。

41. 如权利要求 1 所述的方法,其中步骤 (a) 发生于一个、两个或三个反应器中。

42. 如权利要求 1 所述的方法,其中步骤 (a) 发生于一个反应器中。

涉及基于二盐的热解制程的二氧化碳封存

[0001] 发明背景

[0002] 本申请要求 2012 年 1 月 11 日提交的美国临时专利申请序列第 61/585, 597 号的优先权, 其整体通过引用并入本文。

I. 发明领域

[0003] 本发明通常涉及自诸如发电厂废物流 (例如烟道气) 的来源去除二氧化碳的领域, 从而将第 2 族硅酸盐矿物质转化成第 2 族氯化物盐和 SiO_2 , 并将第 2 族氯化物盐转化成第 2 族氢氧化物和 / 或第 2 族羟基氯化物盐。这些可任选在催化剂的存在下继而与二氧化碳发生反应以形成第 2 族碳酸盐。这些步骤可组合形成循环, 其中以碳酸盐形式封存二氧化碳, 并且将来自一个或多个步骤的副产物, 例如热和化学物质, 在一个或多个其他步骤中再利用或再循环。

II. 相关技术描述

[0005] 大量国内外关注日愈集中于 CO_2 向空气中的排放。具体而言, 注意力已集中于此气体对大气中太阳热的保持的效应 (产生“温室效应”)。尽管关于该效应的大小仍具有一些争论, 但均赞成自点排放源去除 CO_2 (和其他化学物质) 是有益的, 尤其是在进行这种工作的成本足够小的时候。

[0006] 温室气体主要由二氧化碳组成且通过城市发电厂和大规模工业现场发电厂产生, 但其也在任何正常碳燃烧 (例如汽车、雨林开垦、简单燃烧等) 中产生。然而, 其大部分集中点排放发生于地球上的发电厂, 使得从那些固定场所减小或去除成为实现去除技术的吸引点。由于能量产生是温室气体排放的主要原因, 在过去三十年中已着重考察和研究通过各种方式来减小碳强度、改良效率和自发电厂烟道气封存碳等方法。

[0007] 关于封存碳 (呈气态 CO_2 的初始形式) 的尝试已产生许多各种各样的技术, 其通常可分类为地质、陆地或海洋系统。这样的技术的综述提供于 Proceedings of First National Conference on Carbon Sequestration, (2001) 中。迄今为止, 许多 (若非全部) 这些技术消耗过多能量且因此在经济上不可行, 在许多情形下, 所消耗的能量大于通过生成二氧化碳所获得的能量。克服这些缺点中一个或多个缺点的替代方法将是有利的。

[0008] 所提及的缺陷并非意欲穷举, 而是倾向于损害之前已知的用于从废物流去除二氧化碳的技术的效率的多种缺陷中的一些; 然而, 本文所提及的那些缺陷足以表明, 本领域内出现的方法尚未完全令人满意且显著需要本公开所描述和要求保护的技术。

发明简述

[0010] 本文公开了用于二氧化碳封存、包括从废物流去除二氧化碳的方法和装置。

[0011] 在一方面中, 提供了封存由来源产生的二氧化碳的方法, 其包括:

[0012] (a) 使 MgCl_2 或其水合物与水于第一掺合物中在适于形成第一产物混合物的条件下反应, 所述第一产物混合物包含含有 $\text{Mg}(\text{OH})\text{Cl}$ 的第一步骤 (a) 产物和含有 HCl 的第二步骤 (a) 产物;

[0013] (b) 使来自步骤 (a) 的部分或所有 $\text{Mg}(\text{OH})\text{Cl}$ 与一定量的水和一定量的 MgCl_2 于

第二掺合物中在适于形成第二产物混合物的条件下反应,所述第二产物混合物包含含有 $\text{Mg}(\text{OH})_2$ 的第一步骤 (b) 产物和含有 MgCl_2 的第二步骤 (b) 产物,其中水的量足以在所述第二产物混合物中提供大于或等于 6:1 的水与 MgCl_2 的摩尔比;

[0014] (c) 使来自第一步骤 (b) 产物的部分或所有 $\text{Mg}(\text{OH})_2$ 与 CaCl_2 或其水合物以及由所述来源产生的二氧化碳于第三掺合物中在适于形成第三产物混合物的条件下混合,所述第三产物混合物包含含有 MgCl_2 或其水合物的第一步骤 (c) 产物、含有 CaCO_3 的第二步骤 (c) 产物和含有水的第三步骤 (c) 产物;和

[0015] (d) 从所述第三产物混合物分离部分或所有 CaCO_3 ,

[0016] 从而以 CaCO_3 形式封存部分或所有二氧化碳。

[0017] 在某些实施方案中,步骤 (a) 的 MgCl_2 是水合 MgCl_2 (例如 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$)。在一些实施方案中,步骤 (a) 的 MgCl_2 中 90 重量%以上是 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 。在其他实施方案中,在步骤 (b) 和 / 或步骤 (c) 中所形成的部分或所有 MgCl_2 是在步骤 (a) 中所使用的 MgCl_2 。因此,在某些实施方案中,步骤 (a) 中的部分或所有水是以 MgCl_2 水合物形式存在或从步骤 (c) 或步骤 (b) 的水获得。在某些实施方案中,步骤 (a) 中的部分或所有水是以蒸汽或超临界水形式存在。在一些实施方案中,将步骤 (a) 的部分或所有氯化氢与水混合以形成盐酸。在另一实施方案中,第一步骤 (a) 产物包括大于 90 重量%的 $\text{Mg}(\text{OH})\text{Cl}$ 。在某些实施方案中,步骤 (a) 发生于一个、两个或三个反应器中。

[0018] 在一些实施方案中,在步骤 (b) 的第二产物混合物中维持确定量的水。例如,在一些实施方案中,第二产物混合物中水与 MgCl_2 的摩尔比是介于约 6 与约 10 之间、介于约 6 与 9 之间、介于约 6 与 8 之间、介于约 6 与 7 之间或为约 6。在某些实施方案中,方法包括监测第二产物混合物中的 MgCl_2 浓度、第二产物混合物中水的量或监测此二者。在其他实施方案中,基于这样的监测调节步骤 (b) 中的 MgCl_2 和 / 或水的量 (或 MgCl_2 和 / 或水向第二掺合物中的流速)。

[0019] 在另一实施方案中,方法包括分离步骤 (b) 产物。例如,步骤 (b) 的 $\text{Mg}(\text{OH})_2$ 产物可为固体,并且分离步骤 (b) 产物可包括使部分或所有固体 $\text{Mg}(\text{OH})_2$ 与水和 MgCl_2 溶液分离。因此,在一些实施方案中,步骤 (b) 的 MgCl_2 产物是 MgCl_2 水溶液。

[0020] 在又一实施方案中,步骤 (b) 包括使从步骤 (a) 的部分或所有 $\text{Mg}(\text{OH})\text{Cl}$ 与 MgCl_2 和一定量的水于第二掺合物中在适于形成第二产物混合物的条件下反应,所述第二产物混合物包含含有 $\text{Mg}(\text{OH})_2$ 的第一步骤 (b) 产物和含有 MgCl_2 的第二步骤 (b) 产物,其中水的量足以在所述第二掺合物中提供大于或等于 6:1 的水与 Mg 的摩尔比。在一些实施方案中,用于步骤 (b) 的反应的部分或所有 MgCl_2 是步骤 (c) 的 MgCl_2 产物。

[0021] 在另一实施方案中,步骤 (c) 进一步包括在第三掺合物中掺入氢氧化钠盐。

[0022] 在再一实施方案中,方法包括:

[0023] (e) 在适于形成第三产物混合物的条件下掺合硅酸钙矿物质与 HCl ,所述第三产物混合物包含 CaCl_2 、水和二氧化硅。

[0024] 例如,在一些情形下,步骤 (e) 中的部分或所有 HCl 是从步骤 (a) 获得。在某些实施方案中,步骤 (e) 进一步包括将硅酸钙矿物质与 HCl 一起搅动。在一些实施方案中,回收在步骤 (e) 中所生成的部分或所有热。在某些实施方案中,步骤 (c) 的部分或所有 CaCl_2 是步骤 (e) 的 CaCl_2 。在其他实施方案中,方法包括分离步骤,其中从在步骤 (e) 中形成的

CaCl₂ 中去除二氧化硅。在其他实施方案中,步骤 (a) 和 / 或 (b) 的部分或所有水是从步骤 (e) 的水获得的。

[0025] 实施方案的某些方面包括使用硅酸钙矿物质,例如链状硅酸钙。在一些实施方案中,硅酸钙矿物质包括透辉石 (CaMg[Si₂O₆])、透闪石 Ca₂Mg₅{[OH]Si₄O₁₁}₂ 或 CaSiO₃。在一些实施方案中,硅酸钙进一步包括铁硅酸盐 (例如铁橄榄石 (Fe₂[SiO₄])) 和 / 或锰硅酸盐。

[0026] 在一些实施方案中,二氧化碳是呈烟道气形式,其中所述烟道气进一步包含 N₂ 和 H₂O。

[0027] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 200℃ 至约 500℃ 的温度。在一些实施方案中,温度为约 230℃ 至约 260℃。在一些实施方案中,温度为约 250℃。在一些实施方案中,温度为约 200℃ 至约 250℃。在一些实施方案中,温度为约 240℃。

[0028] 在一些实施方案中,步骤 (b) 的适宜反应条件包括约 140℃ 至约 240℃ 的温度。

[0029] 在一些实施方案中,步骤 (c) 的适宜反应条件包括约 20℃ 至约 100℃ 的温度。在一些实施方案中,温度为约 25℃ 至约 95℃。

[0030] 在一些实施方案中,步骤 (e) 的适宜反应条件包括约 50℃ 至约 200℃ 的温度。在一些实施方案中,温度为约 90℃ 至约 150℃。

[0031] 在另一方面中,提供封存由来源产生的二氧化碳的方法,其包括:

[0032] (a) 使第一基于阳离子的卤化物、硫酸盐或硝酸盐或其水合物与水于第一掺合物中在适于形成第一产物混合物的条件下反应,所述第一产物混合物包括第一步骤 (a) 产物和第二步骤 (a) 产物,所述第一步骤 (a) 产物包含第一基于阳离子的氢氧化物盐、第一基于阳离子的氧化物盐和 / 或第一基于阳离子的羟基氯化物盐,所述第二步骤 (a) 产物包含 HCl、H₂SO₄ 或 HNO₃;

[0033] (b) 使部分或所有第一步骤 (a) 产物与第二基于阳离子的卤化物、硫酸盐或硝酸盐或其水合物以及由来源产生的二氧化碳于第二掺合物中在适于形成第二产物混合物的条件下混合,所述第二产物混合物包括第一步骤 (b) 产物、第二步骤 (b) 产物和第三步骤 (b) 产物,所述第一步骤 (b) 产物包含第一基于阳离子的卤化物、硫酸盐和 / 或硝酸盐或其水合物,所述第二步骤 (b) 产物包含第二基于阳离子的碳酸盐,所述第三步骤 (b) 产物包含水;和

[0034] (c) 使部分或所有第二基于阳离子的碳酸盐自第二产物混合物分离,

[0035] 从而将二氧化碳封存成矿物质产物形式。

[0036] 在一些实施方案中,步骤 (a) 的第一基于阳离子的卤化物、硫酸盐或硝酸盐或其水合物是第一基于阳离子的氯化物盐或其水合物,且第二步骤 (a) 产物是 HCl。在一些实施方案中,步骤 (b) 的第一基于阳离子的卤化物、硫酸盐或硝酸盐或其水合物是第一基于阳离子的氯化物盐或其水合物。

[0037] 在一些实施方案中,步骤 (a) 的第一基于阳离子的氯化物盐或其水合物是 MgCl₂。在一些实施方案中,步骤 (a) 的第一基于阳离子的氯化物盐或其水合物是 MgCl₂ 的水合形式。在一些实施方案中,步骤 (a) 的第一基于阳离子的氯化物盐或其水合物是 MgCl₂·6H₂O。在一些实施方案中,步骤 (a) 的第一基于阳离子的氢氧化物盐是 Mg(OH)₂。在一些实施方案中,步骤 (a) 的第一基于阳离子的羟基氯化物盐是 Mg(OH)Cl。在一些实施方案中,第一步骤 (a) 产物主要包括 Mg(OH)Cl。在一些实施方案中,第一步骤 (a) 产物包括大于 90 重量%的

Mg(OH)Cl。在一些实施方案中,第一步骤 (a) 产物是 Mg(OH)Cl。在一些实施方案中,步骤 (a) 的第一基于阳离子的氧化物盐是 MgO。

[0038] 在一些实施方案中,步骤 (b) 的第二基于阳离子的卤化物、硫酸盐或硝酸盐或其水合物是第二基于阳离子的氯化物盐或其水合物,例如 CaCl₂。在一些实施方案中,步骤 (b) 的第一基于阳离子的氯化物盐是 MgCl₂。在一些实施方案中,步骤 (b) 的第一基于阳离子的氯化物盐是 MgCl₂ 的水合形式。在一些实施方案中,步骤 (b) 的第一基于阳离子的氯化物盐是 MgCl₂ · 6H₂O。

[0039] 在一些实施方案中,步骤 (a) 中的部分或所有水以蒸汽或超临界水形式存在。在一些实施方案中,步骤 (a) 的部分或所有水是从步骤 (b) 的水获得。在一些实施方案中,步骤 (b) 进一步包括在第二掺合物中混入氢氧化钠盐。

[0040] 在一些实施方案中,这些方法进一步包括:

[0041] (d) 在适于形成第三产物混合物的条件下掺合第 2 族硅酸盐矿物质与 HCl,所述第三产物混合物包括第 2 族氯化物盐、水和二氧化硅。

[0042] 在一些实施方案中,步骤 (d) 中的部分或所有 HCl 是从步骤 (a) 获得。在一些实施方案中,步骤 (d) 的方法进一步包括将第 2 族硅酸盐矿物质与 HCl 一起搅动。在一些实施方案中,回收在步骤 (d) 中生成的部分或所有热。在一些实施方案中,步骤 (b) 的部分或所有第二基于阳离子的氯化物盐是步骤 (d) 的第 2 族氯化物盐。在一些实施方案中,这些方法进一步包括分离步骤,其中从在步骤 (d) 中形成的第 2 族氯化物盐中去除二氧化硅。在一些实施方案中,步骤 (a) 的部分或所有水是从步骤 (d) 的水获得的。

[0043] 在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括第 2 族链状硅酸盐。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括 CaSiO₃。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括 MgSiO₃。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括橄榄石 (Mg₂[SiO₄])。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括蛇纹石 (Mg₆[OH]₈[Si₄O₁₀])。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括海泡石 (Mg₄[(OH)₂Si₆O₁₅] · 6H₂O)、顽火辉石 (Mg₂[Si₂O₆])、透辉石 (CaMg[Si₂O₆]) 和 / 或透闪石 Ca₂Mg₅[[OH]Si₄O₁₁]₂。在一些实施方案中,第 2 族硅酸盐进一步包括铁硅酸盐和 / 或锰硅酸盐。在一些实施方案中,铁硅酸盐是铁橄榄石 (Fe₂[SiO₄])。

[0044] 在一些实施方案中,在步骤 (b) 中所形成的部分或所有第一基于阳离子的氯化物盐是在步骤 (a) 中使用的第一基于阳离子的氯化物盐。

[0045] 在一些实施方案中,二氧化碳是呈烟道气形式,其中烟道气进一步包含 N₂ 和 H₂O。

[0046] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 200℃ 至约 500℃ 的温度。在一些实施方案中,温度为约 230℃ 至约 260℃。在一些实施方案中,温度为约 250℃。在一些实施方案中,温度为约 200℃ 至约 250℃。在一些实施方案中,温度为约 240℃。

[0047] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 50℃ 至约 200℃ 的温度。在一些实施方案中,温度为约 90℃ 至约 260℃。在一些实施方案中,温度为约 90℃ 至约 230℃。在一些实施方案中,温度为约 130℃。

[0048] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 400℃ 至约 550℃ 的温度。在一些实施方案中,温度为约 450℃ 至约 500℃。

[0049] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 20℃ 至约 100℃ 的温度。在

一些实施方案中,温度为约 25°C 至约 95°C。

[0050] 在一些实施方案中,步骤 (a) 的适宜反应条件包括约 50°C 至约 200°C 的温度。在一些实施方案中,温度为约 90°C 至约 150°C。

[0051] 在另一方面中,本发明提供封存由来源产生的二氧化碳的方法,其包括:

[0052] (a) 将氯化镁盐和水于第一掺合物中在适于形成 (i) 氢氧化镁、氧化镁和 / 或 $\text{Mg}(\text{OH})\text{Cl}$ 以及 (ii) 氯化氢的条件下混合;

[0053] (b) 将 (i) 氢氧化镁、氧化镁和 / 或 $\text{Mg}(\text{OH})\text{Cl}$ 、(ii) CaCl_2 和 (iii) 由来源产生的二氧化碳于第二掺合物中在适于形成 (iv) 碳酸钙、(v) 氯化镁盐和 (vi) 水的条件下混合; 和

[0054] (c) 自第二掺合物分离碳酸钙,从而将二氧化碳封存成矿物质产物形式。

[0055] 在一些实施方案中,将步骤 (a) 的部分或所有氯化氢与水混合以形成盐酸。在一些实施方案中,步骤 (b) (i) 的部分或所有氢氧化镁、氧化镁和 / 或 $\text{Mg}(\text{OH})\text{Cl}$ 是从步骤 (a) (i) 获得的。在一些实施方案中,步骤 (a) 中的部分或所有水是以氯化镁盐的水合物形式存在。在一些实施方案中,步骤 (a) 发生于一个、两个或三个反应器中。在一些实施方案中,步骤 (a) 发生于一个反应器中。在一些实施方案中,步骤 (a) (i) 的氢氧化镁、氧化镁和 / 或 $\text{Mg}(\text{OH})\text{Cl}$ 中 90 重量%以上是 $\text{Mg}(\text{OH})\text{Cl}$ 。在一些实施方案中,氯化镁盐中 90 重量%以上是 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 。

[0056] 在一些实施方案中,这些方法进一步包括:

[0057] (d) 在适于形成第 2 族氯化物盐、水和二氧化硅的条件下掺合第 2 族硅酸盐矿物质与氯化氢。

[0058] 在一些实施方案中,步骤 (d) 中的部分或所有氯化氢是从步骤 (a) 获得的。在一些实施方案中,步骤 (d) 进一步包括将第 2 族硅酸盐矿物质与盐酸一起搅动。在一些实施方案中,步骤 (a) 中的部分或所有氯化镁盐是从步骤 (d) 获得的。在一些实施方案中,所述方法进一步包括分离步骤,其中从在步骤 (d) 中形成的第 2 族氯化物盐中去除二氧化硅。在一些实施方案中,步骤 (a) 的部分或所有水是从步骤 (d) 的水获得的。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括第 2 族链状硅酸盐。

[0059] 在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括 CaSiO_3 。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括 MgSiO_3 。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括橄榄石。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括蛇纹石。在一些实施方案中,步骤 (d) 的第 2 族硅酸盐矿物质包括海泡石、顽火辉石、透辉石和 / 或透闪石。在一些实施方案中,第 2 族硅酸盐进一步包括矿化铁和 / 或锰。

[0060] 在一些实施方案中,步骤 (b) 进一步包括向第二掺合物掺入 CaCl_2 和水。

[0061] 自下列详细描述可明了本公开内容的其他目标、特征和优点。然而,应理解,在指示本发明的具体实施方案时,详细说明和具体实例仅以示例方式给出,因为本领域技术人员从该详细说明可明了本发明的精神和范围内的各种变化和修改。

[0062] 附图简述

[0063] 下列附图形成本说明书的一部分且本说明书包含其以进一步显示本公开内容的某些方面。可通过参照这些附图之一与本文所呈现具体实施方案的详细说明的组合来更好地理解本发明。

[0064] 图 1 是本发明一些实施方案用于以第 2 族碳酸盐形式封存 CO_2 的基于第 2 族氢氧化物的制程的系统的方框图。

[0065] 图 2 是本发明一些实施方案的将 Mg^{2+} 用作催化剂来以碳酸钙形式封存 CO_2 的系统的方框图。

[0066] 图 3 是本文所提供制程的一些实施方案的简化流程图。示出基于第 II 族氢氧化物的制程,其以石灰石(主要由矿物质方解石 CaCO_3 组成)形式封存 CO_2 。此图中的术语“道路用盐”是指第 II 族氯化物,例如 CaCl_2 和 / 或 MgCl_2 ,其中的一种或两种任选地发生水合。在包括 MgCl_2 的实施方案中,可使用热来驱动在道路用盐与水(包含水合的水)之间的反应以形成 HCl 和氢氧化镁 $\text{Mg}(\text{OH})_2$ 和 / 或羟基氯化镁 $\text{Mg}(\text{OH})\text{Cl}$ 。在包括 CaCl_2 的实施方案中,可使用热来驱动在道路用盐与水之间发生反应以形成氢氧化钙和 HCl 。例如,使 HCl 与链状硅酸钙岩石(任选地经研磨)发生反应以形成另外的道路用盐(例如 CaCl_2)和沙(SiO_2)。

[0067] 图 4 是对应于本发明一些实施方案的简化流程图。在本发明一些实施方案中,可使用硅酸盐岩石来以 CaCO_3 形式封存 CO_2 。此图中的术语“道路用盐”是指第 II 族氯化物,例如 CaCl_2 和 / 或 MgCl_2 ,其中的一种或两种任选地发生水合。在道路用盐锅炉中,可使用热来驱动在道路用盐(例如 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)和水(包括水合的水)之间的反应以形成 HCl 和第 II 族氢氧化物、氧化物和 / 或混合氢氧化物-氯化物,包括例如,氢氧化镁 $\text{Mg}(\text{OH})_2$ 和 / 或羟基氯化镁 $\text{Mg}(\text{OH})\text{Cl}$ 。在包括 CaCl_2 的实施方案中,可使用热来驱动在道路用盐与水之间的反应以形成氢氧化钙和 HCl 。 HCl 可出售或使其与硅酸盐岩石(例如链状硅酸盐)反应以形成另外的道路用盐(例如 CaCl_2)和沙(SiO_2)。在这些实施方案中的一些实施方案中,可使用 Mg^{2+} 与 Ca^{2+} 之间的离子交换反应以使得(例如) Mg^{2+} 离子进行循环。

[0068] 图 5 是示出使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。在此实施方案中,将 35% MgCl_2 、65% H_2O 的溶液加热至 536°F (280°C),然后该流以标记为“ $\text{H}_2\text{O}-\text{MgOH}$ ”的流形式离开,其包括 MgCl_2 溶液和固体 $\text{Mg}(\text{OH})_2$ 。通常,在 $\text{Mg}(\text{OH})\text{Cl}$ 溶于水时,其形成 $\text{Mg}(\text{OH})_2$ (固体)和 MgCl_2 (溶解的)。此处, MgCl_2 并不直接用于吸收 CO_2 ,而是将其再循环。净反应是使用便宜原材料 CaCl_2 和水从烟道气捕获 CO_2 以形成 CaCO_3 。模拟结果表明,可有效地再循环 MgCl_2 流,然后使其与 H_2O 和热反应以形成 $\text{Mg}(\text{OH})_2$ 。一种或多种上文所提及化合物随后与 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以最终形成 CaCO_3 ,将其从流中滤出。使最终形成的 MgCl_2 再循环至第一反应器中以重复制程。

[0069] 图 6 是示出使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaCl_2 和水从烟道气捕获 CO_2 以形成 CaCO_3 。在此实施方案中,将六水合物在三个单独室中脱水且在第四室中分解,其中使由分解形成的 HCl 再循环回第三室以防止任何副反应。在这些室中发生的反应包含下列反应:

[0070]

第 1 室: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ 100°C

第 2 室: $\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$ 125°C

第 3 室: $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ 160°C

(存在 HCl 蒸气)

第 4 室: $\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}$ 130°C

将 HCl 再循环至第 3 室。

[0071]

室	反应	典型温度	优选温度范围	注意事项
1 st	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$	100°C	90°C - 120°C	
2 nd	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$	125°C	160°C - 185°C	
3 rd	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$	160°C	190°C - 230°C	*
4 th	$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}$	130°C	230°C - 260°C	**

[0072] * 存在 HCl 蒸气

[0073] ** 使 HCl 蒸气再循环至第 3 室

[0074] 上述前三个反应特征可为脱水作用,而第四反应特征可为分解作用。来自此模拟(于实施例 2 中更详细解释)的结果表明,在较低温度(130-250°C)下, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的分解导致形成 $\text{Mg}(\text{OH})\text{Cl}$ 而非 MgO 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$, 然后 $\text{Mg}(\text{OH})_2$ 与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 发生反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。

[0075] 图 7 是示出使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaCl_2 和水从烟道气捕获 CO_2 以形成 CaCO_3 。在此实施方案中,使六水合镁在两个单独室中脱水且在第三室中分解。脱水 and 分解反应二者均发生于第三室中。不使 HCl 再循环。在这些室中发生的反应包含下列反应:

[0076]

第 1 室: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$ 100°C

第 2 室: $\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$ 125°C

第 3 室: $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + \text{H}_2\text{O}$ 130°C

第 3 室: $\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$ 130°C

[0077]

室	反应	典型温度	优选温度范围	注意事项
1 st	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O}$	100°C	90°C-120°C	
2 nd	$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O}$	125°C	160°C-185°C	
3 rd	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + \text{H}_2\text{O}$	130°C	190°C- 230°C	*
	$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$			

[0078] * 不使 HCl 再循环

[0079] 上述第一、第二和第四反应特征可为脱水作用，而第三反应特征可为分解作用。如图 6 的实施方案中，在此实施方案中所使用的温度导致由 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 形成 $\text{Mg}(\text{OH})\text{Cl}$ 而非 MgO 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ，将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。关于此模拟的另外细节提供于下文实施例 3 中。

[0080] 图 8 是示出使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaCl_2 和水从烟道气捕获 CO_2 以形成 CaCO_3 。此模拟结果表明，其有效地加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 MgO 。 MgO 随后与 H_2O 反应以形成 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ，将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。在此实施方案中，六水合镁在 450°C 下于一个室中同时进行脱水和分解。这是典型温度范围。在一些实施方案中，优选范围为 450°C -500°C。因此完全分解成 MgO 。在此室中所发生的主要反应可如下表示：



[0082] 关于此模拟的另外细节提供于下文实施例 4 中。

[0083] 图 9 是与图 8 实施方案类似的示出使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图，但使 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 在 250°C 的较低温度下于一个室中分解成中间体化合物 $\text{Mg}(\text{OH})\text{Cl}$ 。然后将 $\text{Mg}(\text{OH})\text{Cl}$ 溶于水中以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 随后继续进行与 CaCl_2 和 CO_2 的相同反应以形成 CaCO_3 和 MgCl_2 。在此室中所发生的主要反应可如下表示：



[0085] 在 250°C 下对该反应进行建模。在一些实施方案中，优选范围为 230°C 至 260°C。关于此模拟的另外细节提供于下文实施例 5 中。

[0086] 图 10 示出 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的经加热样品的质量百分比的图表。样品初始质量大约为 70mg 且设定为 100%。在实验期间，在样品热分解的同时测量其质量。使温度迅速斜升 (ramped up) 至 150°C，然后以 0.5°C / 分钟缓慢升高。在大约 220°C 下，重量变得恒定，这与 $\text{Mg}(\text{OH})\text{Cl}$ 的形成一致。

[0087] 图 11 示出对应于实施例 7 的产物的 X 射线衍射数据。

[0088] 图 12 示出对应于来自使用实施例 8 的 $\text{Mg}(\text{OH})_2$ 的反应的产物的 X 射线衍射数据。

[0089] 图 13 示出对应于来自使用实施例 8 的 $\text{Mg}(\text{OH})\text{Cl}$ 的反应的产物的 X 射线衍射数据。

[0090] 图 14 示出温度和压强对 $\text{MgCl}_2 \cdot (\text{H}_2\text{O})$ 分解的影响。

[0091] 图 15 是本文所述 Ca/Mg 制程的实施方案的流程图。

[0092] 图 16 是该 Ca/Mg 制程的变化形式的流程图，其中仅使用镁化合物。在此实施方案

中,并不发生 Ca^{2+} - Mg^{2+} 转变反应。

[0093] 图 17 是该 Ca/Mg 制程的不同变化形式的流程图,其介于先前两个实施方案之间。一半 Mg^{2+} 由 Ca^{2+} 代替,因此制得经矿化的碳酸盐 $\text{MgCa}(\text{CO}_3)_2$ 或白云石。

[0094] 图 18- CaSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ 制程,范例 10 和 11。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaSiO_3 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和 CaCO_3 。此模拟结果表明,其有效地使用来自 HCl 与 CaSiO_3 反应的热和来自天然气或燃煤发电厂排放的烟道气的热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 $\text{Mg}(\text{OH})\text{Cl}$ 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 发生反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。在此实施方案中,在第一室中使用来自 HCl 和 CaSiO_3 反应的热使六水合氯化镁脱水成二水合氯化镁 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 且在 250°C 下于第二室中使用来自烟道气的热将其分解。因此部分地分解成 $\text{Mg}(\text{OH})\text{Cl}$ 。在此室中所发生的主要反应可如下表示:

[0095]

反应	ΔH^{**} kJ/ 摩尔	反应温度范围
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + 5\text{H}_2\text{O} + \text{HCl}$	433	$230^\circ\text{C} - 260^\circ\text{C}$
$2\text{HCl}(\text{g}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	-259	$90^\circ\text{C} - 150^\circ\text{C}$
$2\text{Mg}(\text{OH})\text{Cl} + \text{CO}_2 + \text{CaCl}_2 \rightarrow 2\text{MgCl}_2 + \text{CaCO}_3\downarrow + \text{H}_2\text{O}$	-266	$25^\circ\text{C} - 95^\circ\text{C}$

[0096] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 10 和 11 中。

[0097] 图 19- CaSiO_3 - MgO 制程,范例 12 和 13。此图示出提供使用 AspenPlus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaSiO_3 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和 CaCO_3 。此模拟结果表明,其有效地使用来自 HCl 与 CaSiO_3 反应的热和来自天然气或燃煤发电厂排放的烟道气的热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 MgO 。 MgO 随后与 H_2O 发生反应以形成 $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。在此实施方案中,在第一室中使用来自 HCl 和 CaSiO_3 反应的热使六水合氯化镁脱水成二水合氯化镁 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 且在 450°C 下于第二室中使用来自烟道气的热将其分解。因此完全分解成 MgO 。在此室中所发生的主要反应可如下表示:

[0098]

反应	ΔH kJ/摩尔**	反应温度范围
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgO} + 5\text{H}_2\text{O} + 2\text{HCl}$	560	450 °C – 500 °C
$2\text{HCl}(\text{g}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	-264	90 °C – 150 °C
$\text{MgO} + \text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{CaCO}_3\downarrow$	-133	25 °C – 95 °C

[0099] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 12 和 13 中。

[0100] 图 20-MgSiO₃-Mg(OH)Cl 制程,范例 14 和 15。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 MgSiO₃、CO₂ 和水从烟道气捕获 CO₂ 以形成 SiO₂ 和 MgCO₃。此模拟结果表明,其有效地使用来自 HCl 与 MgSiO₃ 反应的热和来自天然气或燃煤发电厂排放的烟道气的热来分解 MgCl₂ · 2H₂O 以形成 Mg(OH)Cl。Mg(OH)Cl 随后与 H₂O 反应以形成 MgCl₂ 和 Mg(OH)₂, Mg(OH)₂ 随后与来自烟道气的 CO₂ 反应以形成 MgCO₃,将其自流中滤出。将最终形成的 MgCl₂ 再循环至第一反应器中以再次开始制程。在此实施方案中,在 250°C 下使用来自烟道气的热进行分解之前,氯化镁因来自 HCl 和 MgSiO₃ 的热而仍为二水合物形式 MgCl₂ · 2H₂O。因此部分地分解成 Mg(OH)Cl。在此室中所发生的主要反应可如下表示:

[0101]

反应	ΔH kJ/摩尔**	反应温度范围
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[0102]

$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)Cl} + \text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g})$	139.8	230 °C – 260 °C
$2\text{HCl}(\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} + \text{SiO}_2\downarrow$	-282.8	90 °C – 150 °C
$2\text{Mg(OH)Cl} + \text{CO}_2 \rightarrow \text{MgCl}_2 + \text{MgCO}_3\downarrow + \text{H}_2\text{O}$	-193.1	25 °C – 95 °C

[0103] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 14 和 15 中。

[0104] 图 21-MgSiO₃-MgO 制程,范例 16 和 17。此图示出提供使用 AspenPlus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 MgSiO₃、CO₂ 和水从烟道气捕获 CO₂ 以形成 SiO₂ 和 MgCO₃。此模拟结果表明,其有效地使用来自 HCl 与 MgSiO₃ 反应的热和来自天然气或燃煤发电厂排放的烟道气的热来分解 MgCl₂ · 2H₂O 以形成 MgO。MgO 随后与 H₂O 反应以形成 Mg(OH)₂,Mg(OH)₂ 随后与来自烟道气的 CO₂ 反应以形成 MgCO₃,将其自流中滤

出。在此实施方案中,在 450℃下使用来自烟道气的热进行分解之前,氯化镁因来自 HCl 和 MgSiO_3 的热而仍为二水合物形式 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ 。因此完全分解成 MgO 。在此室中所发生的主要反应可如下表示:

[0105]

反应	ΔH kJ/摩尔**	反应温度范围
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2\text{O}(\text{g}) + 2\text{HCl}(\text{g})$	232.9	450 °C – 500 °C
$2\text{HCl}(\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{g}) + \text{SiO}_2\downarrow$	-293.5	90 °C – 150 °C
$\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3\downarrow$	-100	25 °C – 95 °C

[0106] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 16 和 17 中。

[0107] 图 22-透辉石-Mg(OH)Cl 制程,范例 18 和 19。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料透辉石 $\text{MgCa}(\text{SiO}_3)_2$ 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和白云石 $\text{MgCa}(\text{CO}_3)_2$ 。此模拟结果表明,其有效地使用来自 HCl 与 $\text{MgCa}(\text{SiO}_3)_2$ 反应的热和来自天然气或燃煤发电厂排放的烟道气的热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 $\text{Mg}(\text{OH})\text{Cl}$ 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 $\text{MgCa}(\text{CO}_3)_2$, 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。在此实施方案中,在第一室中使用来自 HCl 和 CaSiO_3 反应的热使六水合氯化镁脱水成二水合氯化镁 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 且在 250℃ 下于第二室中使用来自烟道气的热将其分解成 $\text{Mg}(\text{OH})\text{Cl}$ 。在此室中所发生的主要反应可如下表示:

[0108]

反应	ΔH kJ/摩尔**	反应温度范围
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + 5\text{H}_2\text{O}(\text{g}) + \text{HCl}(\text{g})$	433	230°C–260°C
$2\text{HCl}(\text{g}) + \text{MgCa}(\text{SiO}_3)_2 \rightarrow \text{CaCl}_2(\text{aq}) + \text{MgSiO}_3\downarrow + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-235	90°C–150°C
$2\text{HCl}(\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-282.8	90°C–150°C
$4\text{Mg}(\text{OH})\text{Cl} + 2\text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCa}(\text{CO}_3)_2\downarrow + 3\text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}$	-442	25°C–95°C

[0109] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 18 和 19 中。

[0110] 图 23-透辉石-MgO 制程,范例 20 和 21。此图示出提供使用 AspenPlus 制程软件

进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料透辉石 $\text{MgCa}(\text{SiO}_3)_2$ 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和白云石 $\text{MgCa}(\text{CO}_3)_2$ 。此模拟结果表明,其有效地使用来自 HCl 与 $\text{MgCa}(\text{SiO}_3)_2$ 反应的热和来自天然气或燃煤发电厂和 / 或其他热源排放的烟道气的热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 MgO 。 MgO 随后与 H_2O 反应以形成 $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 $\text{MgCa}(\text{CO}_3)_2$, 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。在此实施方案中,在第一室中使用来自 HCl 和 CaSiO_3 反应的热使六水合氯化镁脱水成二水合氯化镁 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, 且在 450°C 下于第二室中使用来自烟道气的热将其分解成 MgO 。在此室中所发生的主要反应可如下表示:

[0111]

反应	ΔH kJ/摩尔**	反应温度范围
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgO} + 5\text{H}_2\text{O} + 2\text{HCl}$	560	$450^\circ\text{C} - 500^\circ\text{C}$
$2\text{HCl}(\text{g}) + \text{MgCa}(\text{SiO}_3)_2 \rightarrow \text{CaCl}_2(\text{g}) + \text{MgSiO}_3\downarrow + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-240	$90^\circ\text{C} - 150^\circ\text{C}$
$2\text{HCl}(\text{aq}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2(\text{aq}) + \text{SiO}_2\downarrow + \text{H}_2\text{O}$	-288	$90^\circ\text{C} - 150^\circ\text{C}$
$2\text{MgO} + 2\text{CO}_2 + \text{CaCl}_2(\text{aq}) \rightarrow \text{MgCa}(\text{CO}_3)_2\downarrow + \text{MgCl}_2(\text{aq})$	-258	$25^\circ\text{C} - 95^\circ\text{C}$

[0112] ** 焓基于反应温度,以及流入反应物和流出产物流的温度。关于此模拟的另外细节提供于下文实施例 20 和 21 中。

[0113] 图 24 说明在以下情形下捕获的 CO_2 百分比:不同烟道气 CO_2 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。参见 $\text{CaSiO}_3\text{-Mg}(\text{OH})\text{Cl}$ 和 $\text{CaSiO}_3\text{-MgO}$ 制程的实施例 10 至 13。

[0114] 图 25 说明在以下情形下捕获的 CO_2 百分比:不同烟道气 CO_2 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。参见 $\text{MgSiO}_3\text{-Mg}(\text{OH})\text{Cl}$ 和 $\text{MgSiO}_3\text{-MgO}$ 制程的实施例 14 至 17。

[0115] 图 26 说明在以下情形下捕获的 CO_2 百分比:不同烟道气 CO_2 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。参见透辉石 $\text{-Mg}(\text{OH})\text{Cl}$ 和透辉石 -MgO 制程的实施例 18 至 21。

[0116] 图 27 是对应于本发明一些实施方案的简化流程图,其中使用两种不同盐(例如 Ca^{2+} 和 Mg^{2+})进行分解和碳酸化。

[0117] 图 28-29 示出 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的经加热样品的质量百分比的图表。样品的初始质量各为约 70mg 且将其各自设定为 100%。在实验期间,在样品热分解的同时测量其质量。将温度斜升至 200°C ,然后在 12 小时运行过程中进一步升高。可通过与所提供的理论稳态进

行比较来确认所分解材料的身份。图 28 是两种曲线的叠加,第一曲线(实线)是时间(分钟)对温度($^{\circ}\text{C}$)的曲线。该线说明温度随时间的斜升;第二曲线(虚线)是重量%(100% = 样品的原始重量)对时间的曲线,其说明样品重量因脱水或分解而随时间减小。图 29 也是两种曲线的叠加,第一曲线(实线)是重量%对温度($^{\circ}\text{C}$)的曲线,其说明样品重量随温度升高而降低;第二曲线(虚线)是重量%相对于温度的导数($\text{wt} \cdot \% / ^{\circ}\text{C}$)对温度($^{\circ}\text{C}$)的曲线。在此值较高时,其表明每度的每一变化的重量损失率较高。若此值为零,则尽管温度仍在增加,但样品重量保持相同,这表明不存在脱水或分解。注意:图 28 和 29 是相同样品。

[0118] 图 30- 在 500°C 下一小时后的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 分解。此图表示出在 500°C 下加热一小时的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的 4 次测试运行的标准化最终和初始重量。一致的最终重量确认,通过在此温度下分解制得 MgO 。

[0119] 图 31- 三室分解。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。在此实施方案中,使用来自冷烟道气的热(室 1)、来自矿物质溶解反应器的热(室 2)和外部天然气(室 3)作为热源。此流程图说明用于分解成 $\text{Mg}(\text{OH})\text{Cl}$ 的三室制程。第一室是通过 200°C 烟道气加热以提供占所需总热约 8.2% 的部分初始热;第二室依赖于自矿物质溶解反应器回收的热来提供分解所需热的 83%,其中 28% 是来自盐酸/硅酸盐矿物质反应且 55% 是来自盐酸的冷凝和形成;且最后第三室使用天然气作为剩余热的外部来源,其占总热的 8.5%。 CO_2 是来自组合循环天然气发电厂,因此可自发电厂获得极少热以为分解反应供能。

[0120] 图 32- 四室分解。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。在此实施方案中,使用来自冷烟道气的热(室 1)、来自另外蒸气的热(室 2)、来自矿物质溶解反应器的热(室 3)和外部天然气(室 4)作为热源。此流程图说明用于分解成 $\text{Mg}(\text{OH})\text{Cl}$ 的四室制程,第一室提供 200°C 烟道气以提供占所需总热约 8.2% 的部分初始热;第二室提供呈额外蒸气形式的热,其占所需总热的 0.8%;第三室依赖于自矿物质溶解反应器回收的热以提供分解所需热的 83%,其中 28% 是来自盐酸/硅酸盐矿物质反应且 55% 是来自盐酸的冷凝和形成;且最后第四室使用天然气作为剩余热的外部来源,其占总热的 8.0%。 CO_2 是来自组合循环天然气发电厂,因此可自发电厂获得极少热为分解反应供能。

[0121] 图 33- 两室分解。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。在此实施方案中,使用来自矿物质溶解反应器的热(室 1)和外部天然气(室 2)作为热源。此流程图说明用于分解成 $\text{Mg}(\text{OH})\text{Cl}$ 的两室制程,第一室依赖于自矿物质溶解反应器回收的热以提供分解所需热的 87%,其中 28% 是来自盐酸/硅酸盐矿物质反应且 59% 是来自盐酸的冷凝和形成;且第二室使用天然气作为剩余热的外部来源,其占总热的 13%。 CO_2 是来自组合循环天然气发电厂,因此可自发电厂获得极少热为分解反应供能。

[0122] 图 34- 两室分解。此图示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。在此实施方案中,使用来自矿物质溶解反应器的热(室 1)和来自开放式循环天然气工厂的热烟道气(室 2)作为热源。此流程图说明用于分解成 $\text{Mg}(\text{OH})\text{Cl}$ 的两室制程,第一室依赖于自矿物质溶解反应器回收的热以提供分解所需热的 87%,其中 28% 是来自盐酸/硅酸盐矿物质反应且 59% 是来自盐酸的冷凝和形成;且第二室使用热烟道气作

为剩余热的外部来源,其占总热的 13%。 CO_2 是来自开放式循环天然气发电厂,因此可自发电厂以 600℃烟道气形式获得大量热为分解反应供能。

[0123] 图 35 示出 Auger 反应器的示意图, Auger 反应器可用于盐分解反应,包含将 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 分解成 $\text{M}(\text{OH})\text{Cl}$ 或 MgO 。这些反应器可包括用于有效热利用的内部加热、用于有效热利用的外部隔热、用于充足固体传输(在存在固体时)的螺杆机构、用于 HCl 去除的充足排气。这类反应器已经用于制备约 1.8kg 的约 90% $\text{Mg}(\text{OH})\text{Cl}$ 。

[0124] 图 36 示出两次使用 Auger 反应器制备 $\text{Mg}(\text{OH})\text{Cl}$ 的单独运行的优化指数。优化指数=转化率% × 效率%。

[0125] 图 37 示出模拟 CaSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ 制程的 Aspen 模型的流程图。

[0126] 图 38A-I 示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaSiO_3 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和 CaCO_3 。使用热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 $\text{Mg}(\text{OH})\text{Cl}$ 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ 。调整 H_2O 的量以有益于形成固体 $\text{Mg}(\text{OH})_2$ 和 MgCl_2 水溶液(将其再循环至第一反应器以再次开始制程)。 $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。A 是该制程的概略图。B-I 是 A 中所示概略图的搭接放大图。

[0127] 图 39A-I 示出提供使用 Aspen Plus 制程软件进行制程模拟的参数和结果的流程图。净反应是使用便宜原材料 CaSiO_3 、 CO_2 和水从烟道气捕获 CO_2 以形成 SiO_2 和 CaCO_3 。使用热来分解 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以形成 $\text{Mg}(\text{OH})\text{Cl}$ 。 $\text{Mg}(\text{OH})\text{Cl}$ 随后与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ 。调整 H_2O 的量以有益于形成固体 $\text{Mg}(\text{OH})_2$ 和 MgCl_2 水溶液(将其再循环至第一反应器以再次开始制程)。 $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。A 是该制程的概略图。B-I 是 A 中所示概略图的搭接放大图。

[0128] 发明详述

[0129] 本发明涉及包括节能制程的二氧化碳封存,其中将第 2 族氯化物转化成第 2 族氢氧化物和氯化氢,然后使用第 2 族氢氧化物和氯化氢从废物流去除二氧化碳。在一些实施方案中,可使氯化氢进一步与第 2 族硅酸盐反应以产生另外的第 2 族氯化物起始材料和二氧化硅。

[0130] 在一些实施方案中,本发明的方法和装置包括一个或多个下列一般组成部分:(1) 使用氯化氢将第 2 族硅酸盐矿物质转化成第 2 族氯化物和二氧化硅,(2) 将第 2 族氯化物转化成第 2 族氢氧化物和氯化氢,(3) 水性去二氧化碳(aqueous decarbonation),从而将气态 CO_2 吸收于包含第 2 族氢氧化物的水性苛性混合物中以形成第 2 族碳酸盐和/或碳酸氢盐产物,和水,(4) 分离制程,从而自液体混合物分离碳酸盐和/或碳酸氢盐产物,(5) 将副产物(包括能量)从一个或多个步骤或制程流再利用或循环至其他的一个或多个步骤或制程流中。这些一般组成部分中的每一个进一步详细解释于下文中。

[0131] 尽管本发明许多实施方案消耗一些能量以实现吸收来自烟道气流的 CO_2 和其他化学物质且实现本文所述的本发明实施方案的其他目标,但本发明某些实施方案的一个优点在于,其提供优于现有技术的生态效率,同时吸收大部分或所有从给定来源(例如发电厂)所排放的 CO_2 。

[0132] 本发明某些实施方案区别于其他 CO₂ 去除制程的另一额外益处在于, 在一些市场条件下, 产物价值远大于所需反应物或净功率或工厂折旧的成本。换言之, 某些实施方案是有益于产生氯-氢-碳酸盐产物的工业方法, 同时实现去除大量所关注的 CO₂ 和附带污染物。

[0133] I. 定义

[0134] 如本文所使用, 术语“碳酸盐”或“碳酸盐产物”通常定义为含有碳酸根基团 [CO₃]²⁻ 的矿物质组分。因此, 这些术语涵盖碳酸盐 / 碳酸氢盐混合物和仅含有碳酸根离子的物质。术语“碳酸氢盐”和“碳酸氢盐产物”通常定义为含有碳酸氢根基团 [HCO₃]¹⁻ 的矿物质组分。因此, 术语涵盖碳酸盐 / 碳酸氢盐混合物和仅含有碳酸氢根离子的物质。

[0135] 如本文中所使用, “Ca/Mg”表示单独的 Ca、单独的 Mg 或 Ca 和 Mg 的混合物。Ca 与 Mg 之比可介于 0:100 至 100:0 之间, 包含 (例如) 1:99、5:95、10:90、20:80、30:70、40:60、50:50、60:40、70:30、80:20、90:10、95:5 和 99:1。符号“Ca/Mg”、“Mg_xCa_(1-x)”和“Ca_xMg_(1-x)”同义。与之相比, “CaMg”或“MgCa”是指该两个离子之比为 1:1。

[0136] 如本文所使用, 术语“生态效率”与术语“热力学效率”同义使用, 且定义为通过本发明某些实施方案所封存的 CO₂ 量 / 所消耗能量 (由式“ $\partial \text{CO}_2 / \partial E$ ”表示), 此值的适当单位为 kWh / 吨 CO₂。以工厂总 CO₂ 的百分比来命名 CO₂ 封存; 类似地以工厂总功率消耗来命名能量消耗。

[0137] 术语“第 II 族”和“第 2 族”可互换使用。

[0138] “六水合物”是指 MgCl₂ · 6H₂O。

[0139] 在使用本发明一些实施方案形成碳酸氢盐和碳酸盐时, 术语“离子比”是指产物中的阳离子除以该产物中存在的碳数的比。因此, 由碳酸氢钙 (Ca(HCO₃)₂) 形成的产物流可视为具有 0.5 的“离子比”(Ca/C), 而由纯碳酸钙 (CaCO₃) 形成的产物流可视为具有 1.0 的“离子比”(Ca/C)。扩展而言, 无限数量的单-、二-和三价阳离子的碳酸盐和碳酸氢盐的连续混合物可视为离子比在 0.5 与 3.0 之间变化。

[0140] 基于上下文, 缩写“MW”意指分子量或兆瓦。

[0141] 缩写“PFD”是流程图。

[0142] 缩写“Q”是热 (或热负荷), 且热是能量中的一种。这并不包含任何其他类型的能量。

[0143] 如本文所使用, 术语“封存”通常用于是指如下技术或实践: 其部分或全部效应是自点排放源去除 CO₂ 且以某一形式储存该 CO₂ 以防止其返回大气中。此术语的应用并不排除视为“封存”技术的所述实施方案的任一形式。

[0144] 在化学式背景下, 缩写“W”是指 H₂O。

[0145] 辉石是在许多火成岩和变质岩中发现的硅酸盐矿物质的集合。其拥有由二氧化硅四面体的单链组成的常见结构且其以单斜和斜方体系结晶。辉石具有通式 XY(Si, Al)₂O₆, 其中 X 表示钙、钠、铁 (II) 和镁且较稀有地为锌、锰和锂, 且 Y 表示具有较小大小的离子, 例如铬、铝、铁 (III)、镁、锰、钪、钛、钒以及甚至铁 (II)。

[0146] 此外, 构成本发明化合物的原子意欲包含这样的原子的所有同位素形式。如本文所使用, 同位素包括那些具有相同原子序数但具有不同质量数的原子。根据一般实例且并不加以限制, 氢同位素包括氕和氘, 且碳同位素包括 ¹³C 和 ¹⁴C。

[0147] 在权利要求书和 / 或说明书中, 词语“一 (a)”或“一 (an)”在与术语“包括”连用时可能意指“一个”, 但也与“一个或多个”、“至少一个”和“一个或一个以上”的含义一致。

[0148] 在本申请中, 术语“约”是用于表明值包括用来测定该值的装置、方法的内在误差变化, 或存在于研究主体之间的变化。

[0149] 术语“包括”、“具有”和“包含”是开放性连系动词。这些动词中的一个或多个的任何形式或时态 (例如“包括 (comprises、comprising)”、“具有 (has、having)”、和“包含 (includes、including)”) 也是开放性。例如, “包括”、“具有”或“包含”一个或多个步骤的任一方法并不限于仅具备该一个或多个步骤且也涵盖其他未列出的步骤。

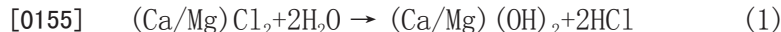
[0150] 在说明书和 / 或权利要求书中使用术语“有效”时, 该术语意指足以实现期望、期待或预期结果。

[0151] 以上述定义替换以引用方式并入本文中的任一参考文献中的任一相冲突的定义。尽管定义了某些术语, 然而, 其不应视为表明未定义的任一术语不明确。相反, 所用的所有术语可视为明确描述本发明以便本领域技术人员可了解本发明的范围且实践本发明。

[0152] II. 使用第 II 族金属的盐封存二氧化碳

[0153] 图 1 示出简化流程图, 其说明本公开内容的装置和方法的一般示例性实施方案。此图仅提供用于解释性目的, 且因此其仅示出本发明的具体实施方案且并不意欲以任一方式限制权利要求书的范围。

[0154] 在图 1 所示的实施方案中, 反应器 10 (例如道路用盐锅炉) 使用功率, 例如外部功率和 / 或再捕获功率 (例如来自热烟道气或外部热源 (例如日光集聚或燃烧) 的热) 来驱动由式 1 表示的反应。



[0156] 此反应中所使用的水可呈液体、蒸汽、结晶水合物 (例如 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) 的形式, 或其可为超临界形式。在一些实施方案中, 该反应使用 MgCl_2 形成 $\text{Mg}(\text{OH})_2$ 和 / 或 $\text{Mg}(\text{OH})\text{Cl}$ (例如参见图 2)。在一些实施方案中, 该反应使用 CaCl_2 形成 $\text{Ca}(\text{OH})_2$ 。可将来自式 1 的部分或所有第 2 族氢氧化物或羟基氯化物 (未展示) 递送至反应器 20。在一些实施方案中, 将部分或所有第 2 族氢氧化物和 / 或第 2 族羟基氯化物以水溶液形式递送至反应器 20。在一些实施方案中, 将部分或所有第 2 族氢氧化物以水性悬浮液形式递送至反应器 20。在一些实施方案中, 将部分或所有第 2 族氢氧化物以固体形式递送至反应器 20。在一些实施方案中, 可将部分或所有氯化氢 (例如以蒸气形式或以盐酸形式) 递送至反应器 30 (例如岩石熔化器)。在一些实施方案中, 将所得第 2 族氢氧化物进一步加热以去除水且形成相应的第 2 族氧化物。在一些变化形式中, 然后可将部分或所有这些第 2 族氧化物递送至反应器 20。

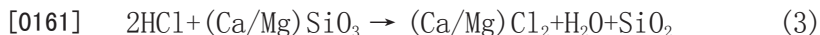
[0157] 可能在首先与废热 /DC 生成系统交换废热之后, 来自来源 (例如烟道气) 的二氧化碳在反应器 20 (例如流化床反应器、喷雾塔去二氧化碳器或去二氧化碳起泡器) 处进入制程。在一些实施方案中, 烟道气的温度为至少 125°C 。第 2 族氢氧化物 (其中的部分或全部可自反应器 10 获得) 与二氧化碳在反应器 20 中根据由式 2 表示的反应发生反应。



[0159] 可将自此反应产生的水递送回反应器 10。通常自反应混合物分离第 2 族碳酸盐。第 2 族碳酸盐具有极低 K_{sp} (溶度积常数)。因此, 使其以固体形式与其他可保持于溶液中的

更可溶的化合物分离。在一些实施方案中,反应通过第 2 族碳酸氢盐进行。在一些实施方案中,生成第 2 族碳酸氢盐且任选地随后将其自反应混合物分离。在一些实施方案中,使第 2 族氧化物(任选地与第 2 族氢氧化物一起或分开地)与二氧化碳发生反应,从而也形成第 2 族碳酸盐。在一些实施方案中,将已去除 CO₂ 和 / 或其他污染物的烟道气释放至空气中。

[0160] 第 2 族硅酸盐(例如 CaSiO₃、MgSiO₃、MgO • FeO • SiO₂ 等)在反应器 30(例如岩石熔化器或矿物质解离反应器)处进入制程。在一些实施方案中,在先前步骤中研磨这些第 2 族硅酸盐。在一些实施方案中,第 2 族硅酸盐是链状硅酸盐。可使这些矿物质与盐酸(呈气体形式或呈盐酸形式,其中的一些或全部可自反应器 10 获得)反应以形成相应的第 2 族金属氯化物(CaCl₂ 和 / 或 MgCl₂)、水和沙(SiO₂)。该反应可由式 3 表示。



[0162] 可将该反应所产生的部分或所有水递送至反应器 10。可将来自式 3 的部分或所有第 2 族氯化物递送至反应器 20。在一些实施方案中,将部分或所有第 2 族氯化物以水溶液形式递送至反应器 20。在一些实施方案中,将部分或所有第 2 族氯化物以水性悬浮液形式递送至反应器 20。在一些实施方案中,将部分或所有第 2 族氯化物以固体形式递送至反应器 20。

[0163] 代表式 1-3 合计的净反应在此处示为式 4:



[0165] 在另一实施方案中,使所得 Mg_xCa_(1-x)CO₃ 封存剂与 HCl 以再生且浓缩 CO₂ 的方式发生反应。使因此形成的 Ca/MgCl₂ 返回分解反应器以产生吸收 CO₂ 的氢氧化物或羟基卤化物。

[0166] 通过图 1 所示和本文所述的制程,生成第 2 族碳酸盐作为来自所捕获 CO₂ 的最终封存剂材料。可循环水、氯化氢和 / 或反应能量中的一些或全部。在一些实施方案中,仅循环这些物质中的一些或并不循环。在一些实施方案中,水、氯化氢和反应能量可用于其他目的。

[0167] 在一些实施方案中且根据给定工厂的烟道气流中的 CO₂ 的浓度,本文所公开的方法可用于仅使用热作为驱动物(没有电损失 (penalty)) 捕获 33-66% 的工厂 CO₂。在一些实施方案中,本文所公开方法的效率通过较低的 CO₂ 浓度而改善,且通过较高(未净化)的烟道气温度而增加。例如,在 320°C 和 7% CO₂ 浓度下,可仅自废热矿化 33% 的烟道气 CO₂。在其他实施方案中,例如在天然气涡轮的出口温度下,可实现大约 100% 矿化。

[0168] 可使用如由本领域技术人员所应用的化学、化工和 / 或材料科学的原理和技术来进一步改良(例如使用模块组件)、优化和扩展(scaled up)这些方法和设备。这些原理和技术教导于例如美国专利 7,727,374、美国专利申请公开 2006/0185985 和 2009/0127127、美国专利申请第 11/233,509 号(2005 年 9 月 22 日提交)、美国临时专利申请第 60/718,906 号(2005 年 9 月 20 日提交)、美国临时专利申请第 60/642,698 号(2005 年 1 月 10 日提交)、美国临时专利申请第 60/612,355 号(2004 年 9 月 23 日提交)、美国专利申请第 12/235,482 号(2008 年 9 月 22 日提交)、美国临时申请第 60/973,948 号(2007 年 9 月 20 日提交)、美国临时申请第 61/032,802 号(2008 年 2 月 29 日提交)、美国临时申请第 61/033,298 号(2008 年 3 月 3 日提交)、美国临时申请第 61/288,242 号(2010 年 1 月 20 日提交)、美国临时申请第 61/362,607 号(2010 年 7 月 8 日提交)和国际申请第 PCT/US08/77122 号(2008

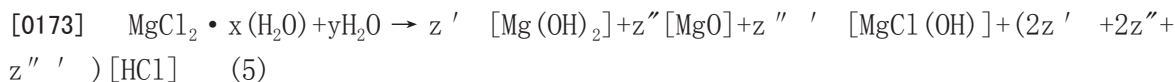
年 9 月 19 日提交)。上文所提及公开内容(包含任一附录)中的每一个的整个文件以引用方式明确并入本文中。

[0169] 包含上述实例以显示本发明的具体实施方案。然而,本领域技术人员借助于本公开内容应了解,在所公开具体实施方案中可实施多种改变且仍可获得相同或类似结果,这并不背离本发明的精神和范围。

[0170] III. 使用 Mg^{2+} 作为催化剂封存二氧化碳

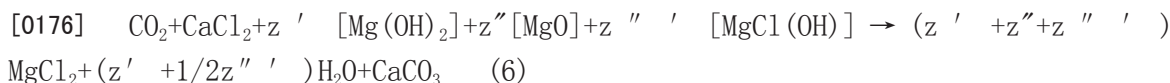
[0171] 图 2 示出简化流程图,其说明本公开内容的装置和方法的一般示例性实施方案。此图仅提供用于解释性目的,且因此其仅示出本发明的具体实施方案且并不意欲以任何方式限制权利要求书的范围。

[0172] 在图 2 中所示的实施方案中,反应器 100 使用功率,例如外部功率和 / 或再捕获功率(例如来自热烟道气的热)来驱动由式 5 表示的分解型反应。



[0174] 此反应中所使用的水可呈氯化镁水合物、液体、蒸汽的形式和 / 或其可为超临界形式。在一些实施方案中,反应可发生于一个、两个、三个或更多个反应器中。在一些实施方案中,反应可以间歇、半间歇或连续制程形式发生。在一些实施方案中,可将部分或所有镁盐产物递送至反应器 200。在一些实施方案中,将部分或所有镁盐产物以水溶液形式递送至反应器 200。在一些实施方案中,将部分或所有镁盐产物以水性悬浮液形式递送至反应器 200。在一些实施方案中,将部分或所有镁盐产物以固体形式递送至反应器 200。在一些实施方案中,可将部分或所有氯化氢(例如以蒸气形式或以盐酸形式)递送至反应器 300(例如岩石熔化器)。在一些实施方案中,将 $Mg(OH)_2$ 进一步加热以去除水且形成 MgO 。在一些实施方案中,将 $MgCl(OH)$ 进一步加热以去除 HCl 且形成 MgO 。在一些变化中,然后将 $Mg(OH)_2$ 、 $MgCl(OH)$ 和 MgO 中的一种或多种递送至反应器 200。

[0175] 可能在首先与废热 / DC 生成系统交换废热之后,来自来源(例如烟道气)的二氧化碳在反应器 200(例如流化床反应器、喷雾塔去二氧化碳器或去二氧化碳起泡器)处进入制程。在一些实施方案中,烟道气的温度为至少 $125^\circ C$ 。使来自反应器 100 的镁盐产物以及 $CaCl_2$ (例如岩石盐)与二氧化碳掺合。二氧化碳与反应器 200 中的镁盐产物和 $CaCl_2$ 根据由式 6 表示的反应发生反应。



[0177] 在一些实施方案中,可将自此反应产生的水递送回反应器 100。通常自反应混合物分离(例如通过沉淀)碳酸钙产物(例如石灰石、方解石)。在一些实施方案中,反应经由镁的碳酸盐和碳酸氢盐进行。在一些实施方案中,反应经由碳酸氢钙盐进行。在一些实施方案中,生成各种第 2 族碳酸氢盐且任选地随后将其自反应混合物分离。在一些实施方案中,任选地在一个或多个进一步纯化和 / 或处理步骤之后,将已去除 CO_2 和 / 或其他污染物的烟道气释放至空气中。在一些实施方案中,使任选地水合的 $MgCl_2$ 产物返回反应器 100。在一些实施方案中,使 $MgCl_2$ 产物在返回反应器 100 之前经历一个或多个分离、纯化和 / 或水合步骤。

[0178] 硅酸钙(例如 $3CaO \cdot SiO_2$ 、 Ca_3SiO_5 ; $2CaO \cdot SiO_2$ 、 Ca_2SiO_4 ; $3CaO \cdot 2SiO_2$ 、 $Ca_3Si_2O_7$ 和

$\text{CaO} \cdot \text{SiO}_2 (\text{CaSiO}_3)$ 在反应器 300 (例如岩石熔化器) 处进入制程。在一些实施方案中, 在先前步骤中研磨这些第 2 族硅酸盐。在一些实施方案中, 第 2 族硅酸盐是链状硅酸盐。在图 2 的实施方案中, 链状硅酸盐是 CaSiO_3 (例如硅灰石, 在一些实施方案中其可自身含有少量铁、镁和 / 或替代铁的锰)。使 CaSiO_3 与氯化氢 (其是气体或呈盐酸形式, 其中的一些或全部可自反应器 100 获得) 反应以形成 CaCl_2 、水和沙 (SiO_2)。该反应可由式 7 表示。

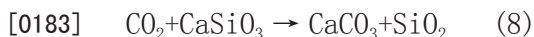


[0180]

反应	ΔH kJ/ 摩尔 **	反应温度范围
$2\text{HCl} (\text{g}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{SiO}_2$	-254	90°C - 150°C
$2\text{HCl} (\text{g}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2 (\text{aq}) + \text{H}_2\text{O} + \text{SiO}_2$	-288	90°C - 150°C

[0181] ** 焓基于反应温度, 以及流入反应物和流出产物流的温度。可将由此反应产生的部分或所有水递送至反应器 100。可将来自式 7 的部分或所有 CaCl_2 递送至反应器 200。在一些实施方案中, 将部分或所有 CaCl_2 以水溶液形式递送至反应器 200。在一些实施方案中, 将部分或所有 CaCl_2 以水性悬浮液形式递送至反应器 200。在一些实施方案中, 将部分或所有 CaCl_2 以固体形式递送至反应器 200。

[0182] 代表式 5-7 总计的净反应在此处示为式 8 :



[0184]

反应	ΔH kJ/ 摩尔 **	ΔG kJ/ 摩尔 **
$\text{CO}_2 + \text{CaSiO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$	-89	-39

[0185] ** 在标准温度和压强 (STP) 下测量。通过图 2 所示和本文所述的制程, 生成碳酸钙作为来自 CO_2 和链状硅酸钙的最终封存剂材料。可循环各种镁盐、水、氯化氢和 / 或反应能量中的一些或全部。在一些实施方案中, 仅循环这些物质中的一些或并不循环。在一些实施方案中, 水、氯化氢和 / 或反应能量可用于其他目的。

[0186] 可使用如由本领域技术人员所应用的化学、化工和 / 或材料科学的原理和技术来进一步改良、优化和扩展这些方法和设备。这些原理和技术教导于例如美国专利 7,727,374、美国专利申请公开 2006/0185985 和 2009/0127127、美国专利申请第 11/233,509 号 (2005 年 9 月 22 日提交)、美国临时专利申请第 60/718,906 号 (2005 年 9 月 20 日提交)、美国临时专利申请第 60/642,698 号 (2005 年 1 月 10 日提交)、美国临时专利申请第 60/612,355 号 (2004 年 9 月 23 日提交)、美国专利申请第 12/235,482 号 (2008 年 9 月 22 日提交)、美国临时申请第 60/973,948 号 (2007 年 9 月 20 日提交)、美国临时申请第 61/032,802 号 (2008 年 2 月 29 日提交)、美国临时申请第 61/033,298 号 (2008 年 3 月 3 日提交)、美国临时申请第 61/288,242 号 (2010 年 1 月 20 日提交)、美国临时申请第 61/362,607 号 (2010 年 7 月 8 日提交) 和国际申请第 PCT/US08/77122 号 (2008 年 9 月 19 日提交)。上文所提及公开内容 (包含任何附录) 中的每一个的整个文件以引用方式明确并入本文中。

[0187] 包含上述实例以显示本发明的具体实施方案。然而,本领域技术人员借助于本公开内容应了解,在所公开具体实施方案中可实施多种改变且仍可获得相同或类似结果,此并不背离本发明的精神和范围。

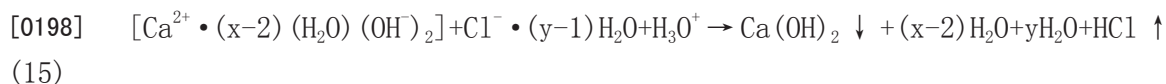
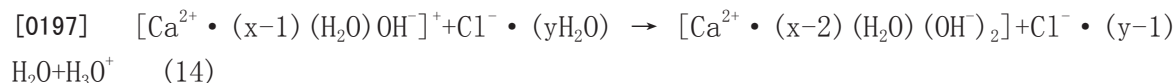
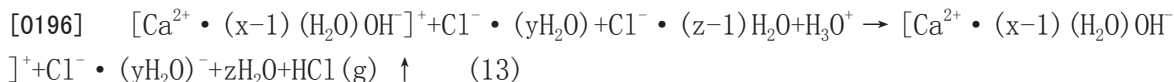
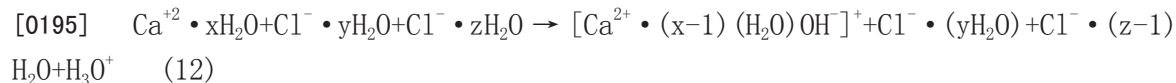
[0188] IV. 使第 2 族氯化物转化成第 2 族氢氧化物或第 2 族羟基氯化物

[0189] 本文公开了使第 2 族氯化物(例如 CaCl_2 或 MgCl_2) 与水发生反应以形成第 2 族氢氧化物、第 2 族氧化物和 / 或混合盐(例如第 2 族氢氧化物氯化物)的制程。这样的反应通常称为分解。在一些实施方案中,水可呈液体、蒸汽形式、来自第 2 族氯化物的水合物,和 / 或其可为超临界形式。蒸汽可来自热交换器,从而来自剧烈燃烧反应(即天然气和氧或氢和氯)的热加热水流。在一些实施方案中,蒸汽也可通过使用工厂或制造厂废热生成。在一些实施方案中,也加热无水或水合的氯化物盐。

[0190] 在 Mg^{2+} 和 Ca^{2+} 的情形下,反应可分别由式 9 和 10 表示:



[0193] ** 在 100°C 下测量。这些反应是吸热的(即,能量),例如必须施加热以使得这些反应发生。这样的能量可自在本文所公开放热制程步骤中的一个或多个生成的废热获得。上述反应可根据多个下列步骤中的一个发生:

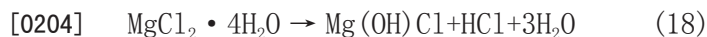


[0199] 在 100°C 下, $\text{CaCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + 2\text{HCl}(\text{g})$ 的反应焓(ΔH)为 284kJ/摩尔 。在一些变化中,使用六水合镁盐 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 。由于在盐的分子结构中并入水,可使用直接加热来引发分解而无需任何其他蒸汽或水。下文示出了用于下列反应的典型反应温度:

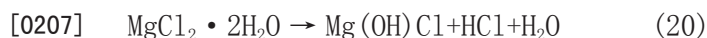
[0200] $95-110^\circ\text{C}$:



[0203] $135-180^\circ\text{C}$:



[0206] $185-230^\circ\text{C}$:



[0208] $>230^\circ\text{C}$:





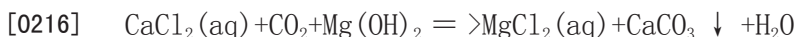
[0212]

反应	参考温度 范围	ΔH kJ/摩尔**	反应温度
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 4\text{H}_2\text{O} + 2 \text{H}_2\text{O}(\text{g})$	95 °C – 110 °C	115.7	100°C
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 2 \text{H}_2\text{O}(\text{g})$	95 °C – 110 °C	134.4	100°C
$\text{MgCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$	135 °C – 180 °C	275	160°C
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}(\text{g})$	135 °C – 180 °C	70.1	160°C
$\text{MgCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{g})$	185 °C – 230 °C	141	210°C
$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O}(\text{g})$	>230 °C	76.6	240°C
$\text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl}(\text{g})$	>230 °C	70.9	240°C
$\text{Mg}(\text{OH})\text{Cl} \rightarrow \text{MgO} + \text{HCl}(\text{g})$	>230 °C	99.2	450°C

[0213] ** 在反应的温度（“反应温度”列）下计算 ΔH 值。参见化学参考文献 Kirk Othmer 4th ed. Vol. 15p. 3431998 John Wiley and Sons, 其以引用方式并入本文。参照下文实施例 1, 提供显示使用便宜原材料 CaCl_2 从烟道气捕获 CO_2 以形成 CaCO_3 的能力的模拟结果, 还参见 Energy Requirements and Equilibrium in the dehydration, hydrolysis and decomposition of Magnesium Chloride - K. K. Kelley, Bureau of Mines 1941 以及 Kinetic Analysis of Thermal Dehydration and Hydrolysis of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ by DTA and TG - Y. Kirsh, S. Yariv 和 S. Shoval - Journal of Thermal Analysis, Vol. 32 (1987), 这二者的全部内容均以引用方式并入本文。

[0214] 在某些方面中, 可通过在 $\text{Mg}(\text{OH})\text{Cl}$ 存在下调节 MgCl_2 与水的比例来更有效地自 MgCl_2 生成 $\text{Mg}(\text{OH})_2$ (经由 $\text{Mg}(\text{OH})\text{Cl}$)。为优化 $\text{Mg}(\text{OH})_2$ 的产生, 调节室中的水量以有利于 $\text{Mg}(\text{OH})_2$ 沉淀, 同时防止形成水合物 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 。具体而言, 将 $\text{Mg}(\text{OH})\text{Cl}$ 溶液中的水量维持于水与 MgCl_2 的摩尔比大于或等于 6, 例如该比介于约 6 与 7 之间。在这些条件下, $\text{Mg}(\text{OH})_2$ 基本上不溶, 而氯化镁保持于水溶液中。例如, 参见 Bakker 2011 的第 52 页, 该文件的全部内容以引用方式并入本文中。

[0215] 因此, 为实现 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 和 $\text{Mg}(\text{OH})_2$ 的产物混合物, 使 $\text{Mg}(\text{OH})\text{Cl}$ 与 MgCl_2 水溶液 (例如来自鼓泡柱的 MgCl_2 水溶液) 反应。该反应为:



[0217] $\text{MgCl}_2(\text{aq})$ 约为 $\text{MgCl}_2 \cdot 13-16\text{H}_2\text{O}$ (液体)

[0218] 煮沸混合物 $\text{MgCl}_2 \cdot 13-16\text{H}_2\text{O}$ (液体) + $\Delta H = >\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (固体) + $7-9\text{H}_2\text{O}$ (气体) ↑ 需要利用大量能量。因此,比 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 更稀释的溶液导致 $\text{Mg}(\text{OH})\text{Cl}$ 歧化, $\text{MgCl}_2 \cdot x\text{H}_2\text{O}$ (液体, 其中 $x \geq 12$) 的溶液也能够导致 $\text{Mg}(\text{OH})\text{Cl}$ 歧化。此式书写如下:

[0219] $\text{Mg}(\text{OH})\text{Cl} + 1/2\text{MgCl}_2 \cdot 13-16\text{H}_2\text{O}$ (液体) = $>1/2\text{Mg}(\text{OH})_2 + \text{MgCl}_2 \cdot 6.5-8\text{H}_2\text{O}$

[0220] 例如:

[0221] $\text{Mg}(\text{OH})\text{Cl} + 1/2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ (液体) = $>1/2\text{Mg}(\text{OH})_2 + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0222] 通过水去除使 $\text{MgCl}_2(\text{aq})$ 重构成原始 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的一半, 且通过添加水从 $\text{Mg}(\text{OH})\text{Cl}$ 歧化形成 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的剩余一半。

[0223] 利用如上文所详述生成的 $\text{Mg}(\text{OH})_2$ 的系统的实例示于图 38A-I 中。Aspen 图如下所述, 且在所定义“水歧化器”周围具有红色矩形。在红色矩形的顶部, $\text{Mg}(\text{OH})\text{Cl}$ (流固体 -1) 离开标记为“分解”(“DECOMP”) 的分解反应器。然后, 在标记为 MGOH2 的模块中, 使 $\text{Mg}(\text{OH})\text{Cl}$ 与来自吸收塔的 MgCl_2 水溶液 (流 - 再循环 2) 混合。其以浆液形式 (流“4”) 自单元离开, 通过热交换器且将热输送至分解室。该流然后称为“13”, 其通过分离单元, 该分离单元将流分离成流 MGCLSLRY (大部分为 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) 和流固体 -2 (其是朝向吸收塔的 $\text{Mg}(\text{OH})_2$)。

[0224] V. 第 2 族氢氧化物与 CO_2 反应形成第 2 族碳酸盐

[0225] 在本公开的另一方面中, 提供用于使用第 2 族氢氧化物、第 2 族氧化物和 / 或第 2 族氢氧化物氯化物作为 CO_2 吸附剂而使二氧化碳源进行去二氧化碳的装置和方法。在一些实施方案中, 使 CO_2 吸收至水性苛性混合物和 / 或溶液中, 其中 CO_2 与氢氧化物和 / 或氧化物盐反应以形成碳酸盐和碳酸氢盐产物。已知各种浓度的氢氧化钠、氢氧化钙和氢氧化镁易于吸收 CO_2 。因此, 在本发明实施方案中, 可使用第 2 族氢氧化物、第 2 族氧化物 (例如 CaO 和 / 或 MgO) 和 / 或其他氢氧化物和氧化物 (例如氢氧化钠) 作为吸收剂。

[0226] 例如, 第 2 族氢氧化物 (例如自第 2 族氯化物获得) 可用于吸附塔以基于下列反应中的一个或两个与 CO_2 反应, 从而捕获 CO_2 :

[0227] $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ (24)

[0228] $\Delta H = -117.92 \text{ kJ/mol}^{**}$

[0229] $\Delta G = -79.91 \text{ kJ/mol}^{**}$

[0230] $\text{Mg}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{H}_2\text{O}$ (25)

[0231] $\Delta H = -58.85 \text{ kJ/mol}^{**}$

[0232] $\Delta G = -16.57 \text{ kJ/mol}^{**}$

[0233] ** 在 STP 下计算。

[0234] 在本发明一些实施方案中, 大部分或几乎所有二氧化碳以此方式反应。在一些实施方案中, 可例如通过去除水 (不论通过连续制程或者不连续制程) 和 / 或通过使碳酸氢盐、碳酸盐或两种类型盐的混合物沉淀来驱动反应完成。参见下文实施例 1, 其提供显示使用源自 CaCl_2 的便宜原材料 $\text{Ca}(\text{CO})_2$ 从烟道气捕获 CO_2 以形成 CaCO_3 的能力的模拟。

[0235] 在一些实施方案中, 最初形成的第 2 族物质可与第二第 2 族氢氧化物发生盐交换反应以转移碳酸根阴离子。例如:

[0236] $\text{CaCl}_2 + \text{MgCO}_3 \rightarrow \text{MgCl}_2 + \text{CaCO}_3$ (25a)

[0237] 可使用由本领域技术人员所应用的化学、化工和 / 或材料科学的原理和技术来进

一步改良、优化和扩展这些方法和设备。这些原理和技术教导于例如美国专利 7, 727, 374、美国专利申请第 11/233, 509 号 (2005 年 9 月 22 日提交)、美国临时专利申请第 60/718, 906 号 (2005 年 9 月 20 日提交)、美国临时专利申请第 60/642, 698 号 (2005 年 1 月 10 日提交)、美国临时专利申请第 60/612, 355 号 (2004 年 9 月 23 日提交)、美国专利申请第 12/235, 482 号 (2008 年 9 月 22 日提交)、美国临时申请第 60/973, 948 号 (2007 年 9 月 20 日提交)、美国临时申请第 61/032, 802 号 (2008 年 2 月 29 日提交)、美国临时申请第 61/033, 298 号 (2008 年 3 月 3 日提交)、美国临时申请第 61/288, 242 号 (2010 年 1 月 20 日提交)、美国临时申请第 61/362, 607 号 (2010 年 7 月 8 日提交) 和国际申请第 PCT/US08/77122 号 (2008 年 9 月 19 日提交)。上文所提及公开内容 (包含任一附录) 中的每一个的整个文件以引用方式明确并入本文中。

[0238] VI. 用于封存二氧化碳的硅酸盐矿物质

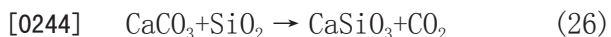
[0239] 在本发明方面中, 提供使用硅酸盐矿物质封存二氧化碳的方法。硅酸盐矿物质构成最大且最重要种类的形成岩石的矿物质之一, 其构成地壳的大约 90%。其是基于其硅酸盐基团的结构进行分类。硅酸盐矿物质均含有硅和氧。在本发明一些方面中, 可使用第 2 族硅酸盐来实现二氧化碳的节能封存。

[0240] 在一些实施方案中, 可使用包含第 2 族链状硅酸盐的组合物。链状硅酸盐, 或链式硅酸盐 (chain silicate), 具有硅酸盐四面体的互锁链, 其含有 SiO_3 (1:3 比率, 对于单链而言) 或 Si_4O_{11} (4:11 比率, 对于双链而言)。

[0241] 在一些实施方案中, 本文所公开的方法使用包括来自辉石基团的第 2 族链状硅酸盐的组合物。例如, 可使用顽火辉石 (MgSiO_3)。

[0242] 在一些实施方案中, 使用包含来自辉石基团的第 2 族链状硅酸盐的组合物。例如, 可使用硅灰石 (CaSiO_3)。在一些实施方案中, 可采用包含第 2 族链状硅酸盐的混合物的组合物, 例如顽火辉石和硅灰石的混合物。在一些实施方案中, 可使用包含混合第 2 族金属链状硅酸盐的组合物, 例如透辉石 ($\text{CaMgSi}_2\text{O}_6$)。

[0243] 硅灰石通常以热变质不纯石灰石的常见成分形式出现。通常, 硅灰石是自方解石与二氧化硅之间的下列反应 (式 26) 得到且失去二氧化碳:



[0245] 在一些实施方案中, 本发明具有有效逆转此天然过程的结果。硅灰石也可在硅卡岩中的扩散反应中产生。其出现在沙石内的石灰石因岩墙而变质时, 此变质使在沙石中因钙离子向外迁移而形成硅灰石。

[0246] 在一些实施方案中, 第 2 族链状硅酸盐组合物的纯度可变化。例如, 在所公开制程中使用的第 2 族链状硅酸盐组合物预计可含有不同量的其他化合物或矿物质 (包括非第 2 族金属离子)。例如, 硅灰石可本身含有少量的铁、镁和锰来替代钙。

[0247] 在一些实施方案中, 可使用包含橄榄石和 / 或蛇纹石的组合物。已尝试利用这些矿物质的 CO_2 矿物质封存方法。Goldberg 等人 (2001) 的技术以引用方式并入本文中。

[0248] 矿物质橄榄石是具有通式 $(\text{Mg}, \text{Fe})_2\text{SiO}_4$ 的硅酸镁铁。在呈宝石品质时, 其称为贵橄榄石。橄榄石出现于镁铁质和超镁铁质火成岩中且在某些变质岩中作为主要矿物质。已知富 Mg 橄榄石自富镁且低二氧化硅的岩浆中发生结晶。在结晶后, 岩浆形成镁铁质岩石, 例如辉长岩和玄武岩。超镁铁质岩石 (例如橄榄岩和纯橄榄岩) 可为在提取岩浆之后留下

的残余物,且通常在提取部分熔化物之后更富有橄榄石。橄榄石和高压结构变化形式占地球上地幔的 50%以上,且橄榄石是地球上最常见的矿物质之一(基于体积)。不纯白云石或其他具有高镁含量和低二氧化硅含量的沉积岩的变质也产生富 Mg 橄榄石或镁橄榄石。

[0249] VII. 从第 2 族硅酸盐生成第 2 族氯化物

[0250] 可使第 2 族硅酸盐(例如 CaSiO_3 、 MgSiO_3 和 / 或本文所公开的其他硅酸盐)与盐酸(呈气体形式或盐酸水溶液形式)反应以形成相应的第 2 族金属氯化物(CaCl_2 和 / 或 MgCl_2)、水和沙。在一些实施方案中,使用在式 1 中所产生的 HCl 以再生式 3 中的 MgCl_2 和 / 或 CaCl_2 。因此产生制程环路。下表 1 示出可单独或组合使用的一些含有钙 / 镁的常见硅酸盐矿物质。已成功地通过使橄榄石和蛇纹石与 HCl 发生反应来进行初始测试。观察到沉淀出 SiO_2 且收集到 MgCl_2 和 CaCl_2 。

[0251] 表 1. 钙 / 镁矿物质

[0252]

矿物质	通式 (标准记法)	通式 (氧化物记法)	比例 第 2 族: SiO_2	比例 第 2 族: 总体
橄榄石	$(\text{Mg,Fe})_2[\text{SiO}_4]$	$(\text{MgO,FeO})_2\cdot\text{SiO}_2$	1:1	1:2
蛇纹石	$\text{Mg}_6[\text{OH}]_8[\text{Si}_4\text{O}_{10}]$	$6\text{MgO}\cdot 4\text{SiO}_2\cdot 4\text{H}_2\text{O}$	3:2	不明确
海泡石	$\text{Mg}_4[(\text{OH})_2\text{Si}_6\text{O}_{15}]6\text{H}_2\text{O}$	$3\text{MgO}\cdot \text{Mg}(\text{OH})_2\cdot 6\text{SiO}_2\cdot 6\text{H}_2\text{O}$	2:3	不明确
顽火辉石	$\text{Mg}_2[\text{Si}_2\text{O}_6]$	$2\text{MgO}\cdot 2\text{SiO}_2$	1:1	不明确
透辉石	$\text{CaMg}[\text{Si}_2\text{O}_6]$	$\text{CaO}\cdot \text{MgO}\cdot 2\text{SiO}_2$	1:1	不明确
透闪石	$\text{Ca}_2\text{Mg}_5\{[\text{OH}]\text{Si}_4\text{O}_{11}\}_2$	$2\text{CaO}\cdot 5\text{MgO}\cdot 8\text{SiO}_2\cdot \text{H}_2\text{O}$	7:8	不明确
硅灰石	CaSiO_3	$\text{CaO}\cdot \text{SiO}_2$	1:1	不明确

[0253] 参见“Handbook of Rocks, Minerals&Gemstones”, Walter Schumann, 1993 年出版, Houghton Mifflin Co •, Boston, New York, 其以引用方式并入本文中。

[0254] VIII. 其他实施方案

[0255] 在一些实施方案中,可通过两种盐来定义二氧化碳至矿物质碳酸盐的转化。第一盐可经加热分解直至其转化为碱(氢氧化物和 / 或氧化物)且排放酸(例如以气体形式)。这种相同的碱与二氧化碳反应以形成碳酸盐、碳酸氢盐或碱性碳酸盐。

[0256] 例如,在一些实施方案中,本公开内容提供如下制程:使来自下表 A-C 的一种或多种盐与水反应以形成氢氧化物、氧化物和 / 或混合氢氧化物卤化物。这样的反应通常称为分解。在一些实施方案中,水可呈液体、蒸汽形式和 / 或来自所选盐的水合物。蒸汽可来自热交换器,从而来自剧烈燃烧反应(即天然气和氧或氢和氯)的热加热水流。在一些实施方案中,蒸汽也可通过使用工厂或制造厂废热生成。在一些实施方案中,也加热无水或水合的卤化物盐。

[0257] 表 A. 分解盐

[0258]

	Li⁺		Na⁺		K⁺		Rb⁺		Cs⁺	
F⁻	NC	N	4747	N	NC	N	10906	N	7490	N
Cl⁻	3876	N	19497	N	8295	N	13616	N	7785	N
Br⁻	3006	N	4336	N	9428	N	13814	N	8196	N
I⁻	6110	N	6044	N	11859	N	9806	N	8196	N

[0259] 表 B. 分解盐 (续)

[0260]

	Mg⁺²		Ca⁺²		Sr⁺²		Ba⁺²	
F⁻	4698	N	3433	N	10346	N	6143	N
Cl⁻	4500*	6W*	5847	2W	9855	6W	8098	2W
Br⁻	5010	6W	2743	N	10346	6W	8114	2W
I⁻	2020	N	4960	N	9855	6W	10890	2W

[0261] * 后续测试已使用加热的样品的 TGA (热重分析) 和温度斜坡设定证明, 反应热在热动力学导出值的 1.5-4% 内。

[0262] 表 C. 分解盐 (续)

[0263]

	Mn⁺²		Fe⁺²		Co⁺²		Ni⁺²		Zn⁺²	
F⁻	3318	N	2101	N	5847	N	5847	N	3285	N

[0264]

Cl⁻	5043	6W	3860	4W	3860	6W	4550	6W	8098	4W
Br⁻	5256	6W	11925	4W	9855	6W	5010	6W	4418	4W
I⁻	5043	6W	3055	4W	4123	6W	5831	6W	4271	4W
SO₄⁻²	NC	4W	13485	4W	3351	4W	8985	6W	8344	7W

[0265] 表 D. 分解盐 (续)

[0266]

	Ag^+		La^{+3}	
F^-	2168	N	13255	7W
Cl^-	5486	N	7490	7W
Br^-	6242	N	5029	7W
I^-	6110	N	4813	7W
SO_4^{-2}	6159	N	10561	6W

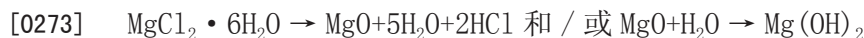
[0267] 对于表 A-D, 数值数据对应于能量 / 所捕获的 CO_2 量 (以 kWh/ 吨表示), NC = 不收敛, 以及 NA = 未获得数据。

[0268] 第一盐的这种相同的碳酸盐、碳酸氢盐或碱性碳酸盐与第二盐反应以进行碳酸盐 / 碳酸氢盐交换, 从而第二盐的阴离子与第一盐的阳离子组合且第二盐的阳离子与第一盐的碳酸根 / 碳酸氢根离子组合, 形成最终的碳酸盐 / 碳酸氢盐。

[0269] 在一些情形下, 源自第一盐的氢氧化物直接与二氧化碳和第二盐反应以形成源自第二盐 (与其阳离子组合) 的碳酸盐 / 碳酸氢盐。在其他情形下, 自反应器室移除源自第一盐 (与其阳离子组合) 的碳酸盐 / 碳酸氢盐 / 碱性碳酸盐且置于第二室中以与第二盐反应。图 27 示出此 2- 盐制程的实施方案。

[0270] 在期望第二金属的盐且此第二金属不能够分解以形成吸收 CO_2 的氢氧化物时, 且若第二盐的碳酸盐 / 碳酸氢盐化合物不溶 (即其自溶液沉淀), 此反应可有益于制备碳酸盐 / 碳酸氢盐。下文是可单独或组合 (包括与本文所论述的一个或多个任一反应组合) 使用的这样的反应的实例的非穷尽性列表。

[0271] 用于分解盐 -1 的实例:



[0274] 去二氧化碳的实例:



[0277] 碳酸盐与盐 -2 的交换实例:



[0281] *在此情形下, 碳酸盐 Na_2CO_3 是盐 -2, 且分解形成 $\text{Ca}(\text{OH})_2$ 的盐 (即 CaCl_2) 是盐 -1。这与碳酸根离子保留于盐 -1 中的一些先前实例相反。

[0282] 已知碳酸盐化合物包含 H_2CO_3 、 Li_2CO_3 、 Na_2CO_3 、 K_2CO_3 、 Rb_2CO_3 、 Cs_2CO_3 、 BeCO_3 、 MgCO_3 、 CaCO_3 、 MgCO_3 、 SrCO_3 、 BaCO_3 、 MnCO_3 、 FeCO_3 、 CoCO_3 、 CuCO_3 、 ZnCO_3 、 Ag_2CO_3 、 CdCO_3 、 $\text{Al}_2(\text{CO}_3)_3$ 、 Ti_2CO_3 、 PbCO_3 和 $\text{La}_2(\text{CO}_3)_3$ 。已知第 IA 族元素是稳定的碳酸氢盐, 例如 LiHCO_3 、 NaHCO_3 、 RbHCO_3 和 CsHCO_3 。第 IIA 族和一些其他元素也可形成碳酸氢盐, 但在一些情形下, 其仅可在溶液中稳定。通常, 形成岩石的元素是 H、C、O、F、Na、Mg、Al、Si、P、S、Cl、K、Ca、Ti、Mg 和 Fe。这些可通过每摩尔吸收 CO_2 的氢氧化物使用最少量的能量来热分解成相应氢氧化物的盐因此可

视为潜在的盐 -1 候选者。

[0283] 基于在表 A-D 中所计算的能量,一些盐具有比 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 更低的能量。下表 E 汇总这些盐和经其使用而相对于 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 降低的损失百分比 (percent penalty)。

[0284] 表 E: 部分较低能量的替代盐

[0285]

化合物	kw-hr/ 吨	降低 %
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	4500	0%
LiCl	3876	16%
LiBr	3006	50%

[0286]

NaBr	4336	4%
MgI_2	2020	123%
CaF_2	3433	31%
CaBr_2	2743	64%
MnF_2	3318	36%
FeF_2	2102	114%
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	3860	17%
$\text{FeI}_2 \cdot 4\text{H}_2\text{O}$	3055	47%
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	3860	17%
$\text{CoI}_2 \cdot 6\text{H}_2\text{O}$	4123	9%
$\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$	3351	34%
$\text{ZnF}_2 \cdot 2\text{H}_2\text{O}$	3285	37%
$\text{ZnBr}_2 \cdot 4\text{H}_2\text{O}$	4418	2%
$\text{ZnI}_2 \cdot 4\text{H}_2\text{O}$	4271	5%
CdF_2	3137	43%
AgF	2168	108%

[0287] 下列盐通过其各别可用的 MSDS 信息而具体规定分解反应。

[0288] 表 F.

[0289]

化合物	分解能量	注意事项
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	4500	
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	5043	仅 Mn^{+2} 形成稳定碳酸盐
$\text{NaI} \cdot 2\text{H}_2\text{O}$	1023	过于罕见
$\text{CoI}_2 \cdot 6\text{H}_2\text{O}$	4123	过于罕见
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	3860	可氧化形成氧化铁, 这将不会形成稳定碳酸盐
LiBr	3006	过于罕见
$\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	1606	留下 Nox
$\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$	3351	有些少见, 留下 SO_3

[0290]

$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$	不可用	毒性副产物
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	2331	留下 NO_2

[0291]

化合物	参考文献
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	http://avogadro.chem.iastate.edu/MSDS/MnCl2.htm
$\text{NaI}_2 \cdot \text{H}_2\text{O}$	http://www.chemicalbook.com/ProductMSDSDetailCB6170714_EN.htm
$\text{CoI}_2 \cdot 6\text{H}_2\text{O}$	http://www.espimetals.com/index.php/msds/527-cobalt-iodide
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	
LiBr	http://www.chemcas.com/material/cas/archive/7550-35-8_v1.asp
$\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	http://avogadro.chem.iastate.edu/MSDS/MgNO3-6H2O.htm
$\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$	http://www.chemicalbook.com/ProductMSDSDetailCB0323842_EN.htm
$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$	http://www.espimetals.com/index.php/msds/460-cadmium-chloride
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	http://avogadro.chem.iastate.edu/MSDS/Ca% 28NO3% 292-4H2O.htm

[0292] IX. 石灰石的生成和用途

[0293] 在本发明方面中,提供以石灰石形式封存二氧化碳的方法。石灰石是主要由矿物质方解石(碳酸钙:CaCO₃)构成的沉积岩。该矿物质具有许多用途,一些用途在下文指出。

[0294] 呈粉末或粉状形式的石灰石(如在本发明一些实施方案中所形成的)可用作土壤改良剂(农业石灰)以中和酸性土壤条件,因此例如中和生态系统中的酸雨效应。上游应用包含使用石灰石作为去硫作用中的试剂。

[0295] 石灰石是用于石工和建筑的重要石料。其优点之一在于其相对易于切成块或更精细的雕刻品。其也具有长效性且耐暴露。石灰石是生石灰、灰浆、水泥和混凝土的关键成分。

[0296] 碳酸钙也用于纸张、塑料、涂料、瓷砖和其他材料的添加剂,其是作为白色颜料和便宜填充剂。碳酸钙的纯化形式可用于牙膏且作为钙源添加至面包和谷物中。CaCO₃也通常在医学上用作抗酸剂。

[0297] 当前,通过采矿或采石来提取在工业中使用的大部分碳酸钙。通过共生成此矿物质(作为在一些实施方案中二氧化碳封存的一部分),本发明提供此重要产物的非提取性来源。

[0298] X. 碳酸镁的生成和用途

[0299] 在本发明方面中,提供以碳酸镁形式封存二氧化碳的方法。碳酸镁MgCO₃是以矿物质形式存在于自然界中的白色固体。最常见碳酸镁形式是称为菱镁矿(MgCO₃)的无水盐,和分别称为二水菱镁矿(MgCO₃·2H₂O)、三水菱镁矿(MgCO₃·3H₂O)和五水菱镁矿(MgCO₃·5H₂O)的二水合物、三水合物和五水合物。碳酸镁具有各种用途;这些用途中的一些在下文中简单讨论。

[0300] 可使用碳酸镁产生镁金属和碱性耐火砖。MgCO₃也用于地板、防火、灭火组合物、化妆品、扑粉和牙膏中。其他应用是作为填充剂材料、塑料中的抑烟剂、氯丁橡胶中的增强剂、干燥剂、轻泻剂和在食物中用于护色。此外,使用高纯度碳酸镁作为抗酸剂且作为食盐中的添加剂以保持其自由流动。

[0301] 当前,通常通过开采矿物质菱镁矿来获得碳酸镁。通过共生成此矿物质(作为在一些实施方案中二氧化碳封存的一部分),本发明提供此重要产物的非提取性来源。

[0302] XI. 二氧化硅的生成和用途

[0303] 在本发明方面中,提供产生作为副产物的二氧化硅的封存二氧化碳的方法。二氧化硅(Silicon dioxide)(也称为二氧化硅(silica))是化学式为SiO₂的硅氧化物且因其硬度而众所周知。二氧化硅最常发现于自然界(以沙或石英形式)以及硅藻细胞壁中。二氧化硅是地壳中的最丰富矿物质。该化合物具有许多用途,这些用途中的一些在下文中简单讨论。

[0304] 二氧化硅主要用于产生窗玻璃、饮用玻璃杯和瓶装饮料。用于电信的大部分光学纤维也是自二氧化硅制得。其是用于许多白色陶瓷(例如陶器、陶石器和瓷器)以及工业波特兰水泥(Portland cement)的主要原材料。

[0305] 二氧化硅是食物生产中的常见添加剂,其中二氧化硅主要用作粉末状食物中的流动剂或用于在吸湿应用中吸收水。在呈水合形式时,二氧化硅以硬质摩擦剂形式用于牙膏中以去除牙菌斑。二氧化硅是硅藻土的主要组分,硅藻土具有自过滤到昆虫控制的许多用途。其也是稻壳灰的主要组分,稻壳灰可用于例如过滤和水泥制造。

[0306] 通过热氧化方法在硅晶圆上生长的二氧化硅薄膜可非常有益于微电子学,其中这些二氧化硅薄膜用作具有高化学稳定性的电绝缘体。在电应用中,其可保护硅,储存电荷,阻断电流,且甚至用作限制电流的受控路径。

[0307] 通常以若干形式来制造二氧化硅,包括玻璃、晶体、凝胶、气溶胶、发烟二氧化硅和胶质二氧化硅。通过共生成此矿物质(作为在一些实施方案中二氧化碳封存的一部分),本发明提供此重要产物的另一来源。

[0308] XII. 产物的分离

[0309] 可采用分离制程从液体溶液和/或反应混合物分离碳酸盐和碳酸氢盐产物。通过操纵碱浓度、温度、压力、反应器尺寸、流体深度和碳酸化程度,可使得出现一种或多种碳酸盐和/或碳酸氢盐的沉淀物。或者,可通过与流入烟道气交换热能自溶液分离碳酸盐/碳酸氢盐产物。

[0310] 根据反应器设计,离开液体流(exit liquid stream)可包含处于不同平衡状态的水、 CaCO_3 、 MgCO_3 、 $\text{Ca}(\text{HCO}_3)_2$ 、 $\text{Mg}(\text{HCO}_3)_2$ 、 $\text{Ca}(\text{OH})_2$ 、 $\text{Ca}(\text{OH})_2$ 、 NaOH 、 NaHCO_3 、 Na_2CO_3 和其他溶解气体。也可发现溶解的痕量排放组分,例如 H_2SO_4 、 HNO_3 和 Hg 。在一实施方案中,从碳酸盐产物去除/分离水涉及添加热能以例如使用再沸器自混合物蒸发水。或者,保持部分碱性溶液且随后在分离室中加热溶液可用于使相对较纯的碳酸盐沉淀至储存罐中且使剩余氢氧化物盐再循环回反应器。在一些实施方案中,随后可将处于平衡浓度和/或呈浆液或浓缩形式的纯碳酸盐、纯碳酸氢盐和此二者的混合物周期性地传输至卡车/罐车。在一些实施方案中,可将液体流转移至蒸发罐/场,其中诸如水等液体可通过蒸发而被带走。

[0311] 气态产物的释放包含担心是否安全地释放氢氧化物或氧化物盐,即,排放“碱雨”。在一些实施方案中,可通过使用简单且便宜的冷凝器/回流单元来防止排放这样的气溶胶化苛性盐。

[0312] 在一些实施方案中,可使用单独地或与水去除制程一起使用的方法来使碳酸盐沉淀。不同碳酸盐平衡状态具有特性范围,其中在升高温度时,给定的碳酸盐(例如 CaCO_3) 将天然沉淀且聚集,这使得适于以浆液形式收回该碳酸盐,且以浆液形式排掉(drawn off)一小部分 NaOH 。

[0313] XIII. 废热的回收

[0314] 因本发明某些实施方案是用于大量排放 CO_2 (呈烟道气或其他来自燃烧制程的热气体(例如出现于发电厂中的那些)的形式)的背景中,故存在充分机会来利用此“废”热以,例如用于将第2族氯化物盐转化成第2族氢氧化物。例如,典型流入烟道气温度(例如,在静电沉淀处理之后)大约为 300°C 。热交换器可将烟道气降低至小于 300°C 的点,同时将水和/或第2族氯化物盐升温以促进此转化。

[0315] 通常,因可在发电厂中获得的烟道气在介于 100°C (通常经净化)、 300°C (在沉淀处理之后)和 900°C (沉淀入口)之间的温度下或在其他这样的温度下离开,因此可通过与功率回收循环(例如氨-水循环(例如“卡利那(Kalina)”循环)、蒸汽循环或任一实现相同热动力学方式的这样的循环)进行热交换以冷却流入烟道气来提取大量经处理的废热。由于本发明一些实施方案依赖于 DC 功率来制造试剂/吸收剂,故可部分地或完全通过废热回收来直接为制程供能,该废热回收是在没有与将 DC 功率转化成 AC 功率以用于其他应用有关的正常变压器损失下实现。另外,通过使用废热工作发动机,可在并不采用发电步骤下

实现显著效率。在一些条件下,发现这些废热回收能量的量可完全为本发明实施方案供能。

[0316] XIV. 替代制程

[0317] 如上所述,本公开内容的装置和方法的一些实施方案自各个反应步骤产生多种有用的中间体、副产物和最终产物,包含氯化氢、第 2 族碳酸盐、第 2 族氢氧化物盐等。在一些实施方案中,这些物质中的一些或全部可用于下文所述的一种或多种方法中。在一些实施方案中,使用下文所概述的一种或多种方法获得上述一个或多个步骤中所采用的起始材料或中间体之一的一些或全部。

[0318] A. 使用氯用于第 2 族硅酸盐的氯化

[0319] 在一些实施方案中,可将氯气液化成盐酸,然后用于将第 2 族硅酸盐矿物质氯化。将氯液化且随后使用盐酸尤其具有吸引力,尤其在氯市场饱和的情形下。可根据式 27 将氯液化:



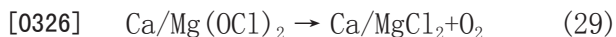
[0321] 在一些实施方案中,可使因此产生的氧返回发电厂本身的空气入口,其中在电力工业研究的整个过程中已显示,富氧入口的工厂具有 (a) 较高卡诺效率 (Carnot-efficiencies), (b) 较浓 CO_2 离开流, (c) 较低热交换以将入口空气升温,和 (d) 其他优于非氧增强的工厂的优点。在一些实施方案中,氧可用于氢 / 氧燃料电池中。在一些实施方案中,氧可用作设计为例如使用氢和天然气的混合物以用于天然气发电的涡轮中的氧化剂部分。

[0322] B. 使用氯用于第 2 族氢氧化物的氯化

[0323] 在一些实施方案中,可使氯气与第 2 族氢氧化物盐反应以得到氯化物和次氯酸盐的混合物 (式 28)。例如, HCl 可作为产物出售且第 2 族氢氧化物盐可用于去除过量氯。



[0325] 然后可使用钴或镍催化剂将第 2 族次氯酸盐分解以形成氧和相应氯化物 (式 29)。



[0327] 然后可回收氯化钙和 / 或氯化镁。

[0328] XV. 从来源去除其他污染物

[0329] 在本发明一些实施方案中,除自来源去除 CO_2 外,去二氧化碳条件也去除 SO_x 和 NO_x , 且以较小程度去除汞。在本发明一些实施方案中, NO_x 、 SO_x 和汞化合物的附带净化 (incidental scrubbing) 可视为具有较大经济意义;即,通过采用本发明实施方案,含有大量这些化合物的煤可在发电厂中燃烧,且在一些实施方案中,所得污染小于在不借助 CO_2 吸收制程下处理的较高级煤。这样的原理和技术教导于例如美国专利 7,727,374、美国专利申请第 11/233,509 号 (2005 年 9 月 22 日提交)、美国临时专利申请第 60/718,906 号 (2005 年 9 月 20 日提交)、美国临时专利申请第 60/642,698 号 (2005 年 1 月 10 日提交)、美国临时专利申请第 60/612,355 号 (2004 年 9 月 23 日提交)、美国专利申请第 12/235,482 号 (2008 年 9 月 22 日提交)、美国临时申请第 60/973,948 号 (2007 年 9 月 20 日提交)、美国临时申请第 61/032,802 号 (2008 年 2 月 29 日提交)、美国临时申请第 61/033,298 号 (2008 年 3 月 3 日提交)、美国临时申请第 61/288,242 号 (2010 年 1 月 20 日提交)、美国临时申请第 61/362,607 号 (2010 年 7 月 8 日提交) 和国际申请第 PCT/US08/77122 号 (2008 年 9 月 19 日提交)。上文所提及公开内容 (包含任一附录) 中的每一个的整个文件以引用方式

明确并入本文中。

实施例

[0330] 包含下列实施例以显示本发明的一些实施方案。本领域技术人员应了解,下列实施例中公开的技术表示发明人发现可良好用于本发明实践的技术,且因此可认为这些技术构成本发明实践的优选方式。然而,本领域技术人员根据本公开内容应了解,在所公开具体实施方案中可实施多种改变且仍可获得相同或类似结果,并不背离本发明的精神和范围。

[0331] 实施例 1- 使用 CaCl_2 从烟道气捕获 CO_2 以形成 CaCO_3 的制程模拟

[0332] 使用 Aspen Plus 7.1 版软件且使用已知反应焓、反应自由能和所定义参数来模拟本发明的一个实施方案,从而测定用于利用 CaCl_2 和热从烟道气流捕获 CO_2 以形成 CaCO_3 产物的质量和能量平衡及适宜的条件。这些结果表明,可使用便宜原材料、 CaCl_2 和水从烟道气捕获 CO_2 , 以形成 CaCO_3 。

[0333] 所定义参数部分包含图 5 中所示的流程图。模拟结果表明,可有效地再循环 MgCl_2 流以与 H_2O 和热发生反应以形成 $\text{Mg}(\text{OH})_2$ 。此 $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 , 将其自流中滤出。将最终形成的 MgCl_2 再循环至第一反应器以再次开始制程。此制程并不限于用于 CaCl_2 的任一特定源。例如,其可通过使硅酸钙与 HCl 反应以得到 CaCl_2 来获得。

[0334] 指定用于此模拟的限制和参数包括:

[0335] • 反应是以 100% 效率运行且并无损失。在试运行测定反应效率时,可修改模拟。

[0336] • 模拟并不考虑 CaCl_2 原料或所需的任一补充 MgCl_2 (因来自系统的损失) 中的杂质。

[0337] 此模拟结果表明,初步净能量消耗大约为 130MM Btu/hr。表 2a 和 2b 提供关于模拟制程的各种流(表中的列)的质量和能量。每一流对应于图 5 的流。

[0338] 制程由两个主要反应区段和一个固体过滤区段组成。第一反应器加热 MgCl_2 / 水溶液以使其分解成 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流和 $\text{Mg}(\text{OH})_2$ 液体流。将 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流输送至 HCl 吸收塔。将 $\text{Mg}(\text{OH})_2$ 溶液输送至反应器 2 用于进一步处理。此反应器的化学反应可由下式表示:



[0340] 将 CaCl_2 溶液和烟道气流添加至反应器 2 中的 MgCl_2 中。此反应形成 CaCO_3 、 MgCl_2 和水。 CaCO_3 发生沉淀且在过滤器或倾析器中移除。将剩余 MgCl_2 和水再循环至第一反应器。添加额外的水以完成第一反应器所需的水平衡。此反应器的化学反应可由下式表示:



[0342] 此制程的主要进料是 CaCl_2 、烟道气(CO_2) 和水。使用、再形成且再循环该系统中的 MgCl_2 。仅使用所需补充 MgCl_2 来代替与 CaCO_3 产物一起离开系统的少量 MgCl_2 和与 $\text{HCl}/$ 水产物一起离开的少量 MgCl_2 。

[0343] 此制程消耗净能量。存在交叉热交换以回收高温流中的热,从而预加热进料流。可通过使因此形成的浓 HCl 与硅酸盐矿物质进行反应来获得显著的热回收率。

[0344]

表 2a. 关于模拟使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的质量和能量。

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
温度 F	485.8	151.6	250	95	77	95	104	77	536
压强 psia	15	15	15	15	15	15	15	15	15
蒸气分率	0	0	0.025	0	0		1	0	0
摩尔流速 lbmol/hr	1594.401	7655.248	7653.691	3568.272	139.697	139.502	611.154	2220.337	1594.401
质量流速 lb/hr	53195.71	162514.8	162514.8	115530.1	15504	13962.37	19206	40000	53195.71
体积流速 gal/min	38.289	238.669	12389.12	114.43	14.159		30680.73	80.111	40.178
焓 MMBtu/hr	-214.568	-918.028	-909.155	-574.405	-47.795		-27.903	-273.013	-205.695
H ₂ O	1473.175	105624.1	105603	33281.39			750.535	40000	1473.172
H ₂									
Cl ₂									
HCl	痕量	痕量	0.001	痕量					痕量
CO ₂		<0.001	0.091	0.005			6158.236		
CO									
O ₂		0.055	0.055	0.055			2116.894		
N ₂		0.137	0.137	0.137			10180.34		
CaCl ₂					15504				

[0345]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		7.797	痕量	7.797					
Mg ²⁺	11114.84	14507.52	14506.86	11942.37					11115.59
H ⁺	< 0.001	痕量	痕量	痕量				痕量	< 0.001
CaOH ⁺		< 0.001	痕量	< 0.001					
MgOH ⁺	22.961	15.364	17.613	25.319					20.435
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				21433.25					

[0346]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				13962.37		13962.37			
MgCO ₃ (s)		0.174							
CaCl ₂ -6W			42.623						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	8137.518	7.043	5.576	0.08					8139.306
ClO ⁻									
HCO ₃ ⁻		0.001	< 0.001	0.119					
Cl ⁻	32447.21	42352.6	42338.81	34877.24					32447.21
OH ⁻	< 0.001	0.001	0.001	< 0.001				< 0.001	< 0.001
CO ₃ ²⁻		痕量	痕量	0.001					
H ₂ O	0.028	0.65	0.65	0.288			0.039	1	0.028

[0347]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
H ₂									
Cl ₂									
HCl	痕量	痕量	3 PPB	痕量					痕量
CO ₂		痕量	563 PPB	40 PPB			0.321		
CO									
O ₂		336 PPB	336 PPB	473 PPB			0.11		
N ₂		844 PPB	844 PPB	1 PPM			0.53		
CaCl ₂					1				
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		48 PPM	痕量	67 PPM					

[0348]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Mg ²⁺	0.209	0.089	0.089	0.103					0.209
H ⁺	1 PPB	痕量	痕量	痕量				痕量	5 PPB
CAOH ⁺		1 PPB	痕量	1 PPB					
MgOH ⁺	432 PPM	95 PPM	108 PPM	219 PPM					384 PPM
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				0.186					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				0.121		1			
MgCO ₃ (s)		1 PPM							
CaCl ₂ -6W			262 PPM						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									

[0349]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	0.153	43 PPM	34 PPM	691 PPB					0.153
ClO ⁻									
HCO ₃ ⁻		5 PPB	痕量	1 PPM					
Cl ⁻	0.61	0.261	0.261	0.302					0.61
OH ⁻	痕量	6 PPB	6 PPB	痕量				2 PPB	痕量
CO ₃ ²⁻		痕量	痕量	12 PPB					
H ₂ O	81.774	5863.026	5861.857	1847.398			41.661	2220.337	81.773
H ₂									
Cl ₂									
HCl	痕量	痕量	<0.001	痕量					痕量
CO ₂		痕量	0.002	<0.001			139.929		
CO									
O ₂		0.002	0.002	0.002			66.155		
N ₂		0.005	0.005	0.005			363.408		
CaCl ₂					139.697				
Ca(OH) ₂									

[0350]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		0.195	痕量	0.195					
Mg ²⁺	457.328	596.922	596.894	491.376				457.358	
H ⁺	< 0.001	痕量	痕量	痕量				痕量	< 0.001
CAOH ⁺		痕量	痕量	痕量					
MgOH ⁺	0.556	0.372	0.426	0.613					0.495
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				105.426					
MgCl ₂ -4W									

[0351]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
CaCl ₂ (s)									
CaCO ₃ (s)				139.502		139.502			
MgCO ₃ (s)		0.002							
CaCl ₂ -6W			0.195						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									
Mg(OH) ₂ (s)	139.533	0.121	0.096	0.001					139.564
ClO ⁻									
HCO ₃ ⁻		< 0.001	痕量	0.002					
Cl ⁻	915.211	1194.604	1194.215	983.753					915.211
OH ⁻	痕量	< 0.001	< 0.001	痕量				痕量	痕量
CO ₃ ²⁻		痕量	痕量	< 0.001					
H ₂ O	0.051	0.766	0.766	0.518			0.068	1	0.051
H ₂									

[0352]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Cl ₂									
HCl	痕量	痕量	2 PPB	痕量					痕量
CO ₂		痕量	271 PPB	29 PPB			0.229		
CO									
O ₂		223 PPB	223 PPB	478 PPB			0.108		
N ₂		640 PPB	640 PPB	1 PPM			0.595		
CaCl ₂					1				
Ca(OH) ₂									
CaCO ₃									
Mg(OH) ₂									
Mg(OH)Cl									
MgCl ₂									
MgCO ₃									
Ca(O)Cl ₂									
CaCl ₂ O ₂									
Ca ²⁺		25 PPM	痕量	55 PPM					
Mg ²⁺	0.287	0.078	0.078	0.138					0.287

[0353]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
H ⁺	49 PPB	痕量	痕量	痕量				2 PPB	156 PPB
CaOH ⁺		痕量	痕量	痕量					
MgOH ⁺	349 PPM	49 PPM	56 PPM	172 PPM					310 PPM
HClO									
MgCO ₃ -3W									
MgCl ₂ (s)									
MgCl ₂ -6W				0.03					
MgCl ₂ -4W									
CaCl ₂ (s)									
CaCO ₃ (s)				0.039		1			
MgCO ₃ (s)		269 PPB							
CaCl ₂ -6W			25 PPM						
CaCl ₂ -4W									
CaCl ₂ -2W									
MgCl ₂ -2W									
MgCl ₂ -W									
Ca(OH) ₂ (s)									

[0354]

[0355]

制程流名称→	1	2	3	底部残余物	CaCl ₂	CaCO ₃	FG-IN	H ₂ O	H ₂ O-MgOH
Mg(OH) ₂ (s)	0.088	16 PPM	12 PPM	383 PPB					0.088
ClO ⁻									
HCO ₃ ⁻		2 PPB	痕量	547 PPB					
Cl ⁻	0.574	0.156	0.156	0.276					0.574
OH ⁻	1 PPB	8 PPB	7 PPB	痕量				2 PPB	1 PPB
CO ₃ ²⁻		痕量	痕量	6 PPB					
PH	5.319	6.955	5.875	7.557				6.999	5.152

表 2b. 关于模拟使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的质量和能量。

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
温度 F	77	536	250	286.8	95	95
压强 psia	15	15	15	15	15	15
蒸气分率	0	1	0.025	0.021	0	1
摩尔流速 lbmol/hr	3383.073	5781.846	7655.866	3814.738	3427.371	433.305
质量流速 lb/hr	60947	109319.3	162515	93195.71	101567.8	12375.59
体积流速 gal/min	122.063	512251.6	12240.14	5364.891	104.123	21428.56
焓 MMBtu/hr	-415.984	-561.862	-909.177	-487.581	-502.044	-0.364

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
H ₂ O	60947	99124.11	105634.7	41473.17	33262.52	59.861
H ₂						
Cl ₂						
HCl		10195.18	0.087	0.009	痕量	痕量
CO ₂					痕量	18.689
CO						
O ₂					0.055	2116.839
N ₂					0.137	10180.2
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						

[0356]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
Ca ²⁺					7.797	
Mg ²⁺			14519.48	11116.3	11938.09	
H ⁺	痕量		< 0.001	痕量	痕量	
CaOH ⁺					< 0.001	
MgOH ⁺			0.112	17.999	25.309	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					21468.81	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					0.175	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						

[0357]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				8141.025	0.024	
ClO ⁻						
HCO ₃ ⁻					痕量	
Cl ⁻			42360.62	32447.2	34864.84	
OH ⁻	< 0.001		痕量	< 0.001	< 0.001	
CO ₃ ²⁻					痕量	
Mass Frac						
H ₂ O	1	0.907	0.65	0.445	0.327	0.005
H ₂						
Cl ₂						
HCl		0.093	534 PPB	92 PPB	痕量	痕量
CO ₂					痕量	0.002
CO						
O ₂					538 PPB	0.171
N ₂					1 PPM	0.823

[0358]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					77 PPM	
Mg ²⁺			0.089	0.119	0.118	
H ⁺	痕量		2 PPB	痕量	痕量	
CaOH ⁺					1 PPB	
MgOH ⁺			689 PPB	193 PPM	249 PPM	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						

[0359]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
MgCl ₂ -6W					0.211	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					2 PPM	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				0.087	240 PPB	
ClO ⁻						
HCO ₃ ⁻					痕量	
Cl ⁻			0.261	0.348	0.343	
OH ⁻	2 PPB		痕量	2 PPB	痕量	
CO ₃ ²⁻					痕量	

[0360]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
H ₂ O	3383.073	5502.224	5863.617	2302.111	1846.35	3.323
H ₂						
Cl ₂						
HCl		279.622	0.002	< 0.001	痕量	痕量
CO ₂					痕量	0.425
CO						
O ₂					0.002	66.154
N ₂					0.005	363.404
CaCl ₂						
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						

[0361]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
Ca ²⁺					0.195	
Mg ²⁺			597.414	457.388	491.201	
H ⁺	痕量		< 0.001	痕量	痕量	
CaOH ⁺					痕量	
MgOH ⁺			0.003	0.436	0.613	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					105.601	
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					0.002	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						

[0362]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				139.593	<0.001	
ClO ⁻						
HCO ₃ ⁻					痕量	
Cl ⁻			1194.83	915.211	983.403	
OH ⁻	痕量		痕量	痕量	痕量	
CO ₃ ²⁻					痕量	
H ₂ O	1	0.952	0.766	0.603	0.539	0.008
H ₂						
Cl ₂						
HCl		0.048	311 PPB	62 PPB	痕量	痕量
CO ₂					痕量	980 PPM
CO						
O ₂					498 PPB	0.153
N ₂					1 PPM	0.839
CaCl ₂						

[0363]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
Ca(OH) ₂						
CaCO ₃						
Mg(OH) ₂						
Mg(OH)Cl						
MgCl ₂						
MgCO ₃						
Ca(O)Cl ₂						
CaCl ₂ O ₂						
Ca ²⁺					57 PPM	
Mg ²⁺				0.12	0.143	
H ⁺	2 PPB		0.078	痕量	痕量	
CaOH ⁺			43 PPB	痕量	痕量	
MgOH ⁺			354 PPB	114 PPM	179 PPM	
HClO						
MgCO ₃ -3W						
MgCl ₂ (s)						
MgCl ₂ -6W					0.031	

[0364]

制程流名称→	H ₂ O-IN	HCl-H ₂ O	Mg-CaCl ₂	MgOH-O1	返回	RX3 通气孔
MgCl ₂ -4W						
CaCl ₂ (s)						
CaCO ₃ (s)						
MgCO ₃ (s)					607 PPB	
CaCl ₂ -6W						
CaCl ₂ -4W						
CaCl ₂ -2W						
MgCl ₂ -2W						
MgCl ₂ -W						
Ca(OH) ₂ (s)						
Mg(OH) ₂ (s)				0.037	122 PPB	
ClO ⁻						
HCO ₃ ⁻					痕量	
Cl ⁻			0.156	0.24	0.287	
OH ⁻	2 PPB		痕量	2 PPB	痕量	
CO ₃ ²⁻					痕量	
PH	6.999		3.678	5.438	7.557	

[0365] 实施例 2(范例 1)– 镁离子催化的使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的制程模拟。

[0366] 模拟结果表明,可有效地在三个单独脱水反应(各自在其独立的室中)中加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 流,随后进行分解反应(也在其独立的室中),从而形成 $\text{Mg}(\text{OH})\text{Cl}$ 和 HCl ,即总共 4 个室。使 $\text{Mg}(\text{OH})\text{Cl}$ 与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ,将其自流中滤出。将最终形成的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以及早期产物再循环至第一反应器以再次开始制程。

[0367] 此制程并不限于用于 CaCl_2 的任一特定源。例如,其可通过使硅酸钙与 HCl 反应以得到 CaCl_2 来获得。

[0368] 指定用于此模拟的限制和参数包括:

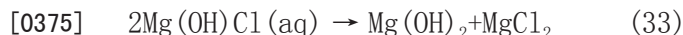
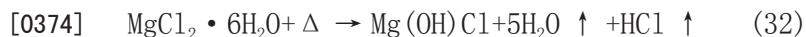
[0369] • 反应是以 100%效率运行且并无损失。在试运行测定反应效率时,可修改模拟。

[0370] • 模拟并不考虑 CaCl_2 原料或所需的任一补充 MgCl_2 (因来自系统的损失)中的杂质。

[0371] • 所定义参数的一部分包括图 6 所示的流程图。

[0372] 此模拟结果表明,初步净能量消耗为 5946kwh/吨 CO_2 。表 3 提供关于模拟制程的各种流的质量和能量。每一流对应于图 6 的流。

[0373] 制程由两个主要反应器和一个固体过滤区段组成。第一反应器加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以使其分解成 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流和 $\text{Mg}(\text{OH})\text{Cl}$ 固体流。将 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流输送至热交换器以回收额外热。将自 $\text{Mg}(\text{OH})\text{Cl}$ 形成的 $\text{Mg}(\text{OH})_2$ 输送至反应器 2 以用于进一步处理。在此反应器中发生的化学反应包括如下:



[0376] 将 CaCl_2 溶液和烟道气流添加至反应器 2 中的 $\text{Mg}(\text{OH})_2$ 中。此反应形成 CaCO_3 、 MgCl_2 和水。 CaCO_3 发生沉淀且在过滤器或倾析器中移除。将剩余 MgCl_2 和水再循环至第一反应器中。添加额外的水以完成第一反应器所需的水平衡。在此反应器中发生的化学反应包括如下:



[0378] 此制程的主要进料是 CaCl_2 、烟道气(CO_2)和水。使用、再形成且再循环系统中的 MgCl_2 。仅使用所需补充 MgCl_2 来代替与 CaCO_3 产物一起离开系统的少量 MgCl_2 和与 $\text{HCl}/$ 水产物一起离开的少量 MgCl_2 。

[0379] 此制程消耗净能量。研究能量的量并优化。存在交叉热交换以回收高温流中的热,从而预加热进料流。

[0380] 用于此制程(范例 1)的步骤汇总于下文中:

[0381]

范例 1			
3 步骤脱水，然后分解			
在 3 个单独室中使六水合物脱水。步骤 1 为从六水合物到四水合物，步骤 2 为从四水合物到二水合物，步骤 3 为从二水合物到单水合物。单水合物在第四室中分解成 80% Mg(OH)Cl、20% MgCl ₂ 。			
吸收的 CO ₂	53333	MTPY	
CaCl ₂	134574	MTPY	
无水 HCl	88368	MTPY	
CaCO ₃	105989	MTPY	
再循环的六水合物	597447	MTPY	
六水合物到四水合物(100 °C)	1757	kWh/吨 CO ₂	
四水合物到二水合物(125C °)	2135	kWh/吨 CO ₂	
二水合物到单水合物(160 °C & HCl PP)	1150	kWh/吨 CO ₂	
分解(130 °C)	1051	kWh/吨 CO ₂	
成 80% Mg(OH)Cl 20% MgCl ₂			
得到 90% HCl 蒸气			
	0.9	MW	
从 28% HCl 蒸气回收热	148	kWh/吨 CO ₂	
总计	5946	kWh/吨 CO ₂	

[0382]

表 3a. 关于范例 1 模拟的质量和能量。

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl 蒸气
温度 C	25	95	104	25	100	125	160	130
压强 psia	14.7	14.7	15.78	14.7	16.166	16.166	16.166	14.696
质量蒸气分率	0	0	1	0	1	1	1	1
质量固体分率	1	1	0	0	0	0	0	0
质量流速 吨/年	134573.943	121369.558	166332.6	290318.99	105883.496	105890.399	17179.526	97647.172
体积流速 gal/min	30.929	22.514	76673.298	8099.644	82228.086	87740.919	10242.935	48861.42
焓 MW	-30.599	-46.174	-17.479	-146.075	-44.628	-44.47	-3.258	-10.757
密度 lb/cuft	136.522	169.146	0.068	1.125	0.04	0.038	0.053	0.063
H ₂ O	0	0	6499.971	290318.99	105883.496	105885.779	5681.299	9278.695
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	4.62	11498.227	88368.477
CO ₂	0	0	53333.098	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0	0

[0383]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl 蒸气
CaCl ₂	134573.943	80.499	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	1	1	0.331	0.095
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0

[0384]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl 蒸气
HCl	0	0	0	0	0	0	0.669	0.905
CO ₂	0	0	0.321	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0	0
N ₂	0	0	0.53	0	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0

[0385]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl 蒸气
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	11.441	511.008	186.372	186.376	10	16.332
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0.004	10	76.854
CO ₂	0	0	38.427	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0	0
N ₂	0	0	99.8	0	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0

[0386]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl-PP	HCl 蒸气
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0

表 3b. 关于范例 1 模拟的质量和能量。

制程流名称→	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔浆液	固体-1	固体-2	蒸气
温度 °C	125	100	104	95	95	160	130	160
压强 psia	16.166	16.166	14.696	14.7	14.7	22.044	14.696	22.044
质量蒸气分率	0	0	0	0	1	0	0	1
质量固体分率	1	1	1	0.998	0	1	1	0
质量流速 吨/年	385672.688491563.087597446.583598447.468	106499.178	719817.026332737.843235090.67170114.371					
体积流速 gal/min	39.902	39.902	116.892	147.062	167.321	39.902	43.473	42506.729
焓 MW	-117.767	-175.272	-230.554	-231.312	-277.487	-88.626	-71.431	-25.379

[0387]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔浆液	固体-1	固体-2	蒸气
密度 lb/cuft	303.274	386.542	160.371	127.684	0.059	261.649	169.678	0.052
H ₂ O	0	0	0	1000	0	0	0	58620.764
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	11493.607
CO ₂	0	0	0	0	0.532	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0	0.165	18333.088	0	0	0
N ₂	0	0	0	0.72	88165.558	0	0	0
CaCl ₂	0	0	0	0	80.499	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	121289.059	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	49037.72	0
MgCl ₂ *W	0	0	0	0	0	332737.843	0	0
MgCl ₂ *2W	385662.96	0	0	0	0	0	0	0

[0388]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔浆液	固体-1	固体-2	蒸气
MgCl ₂ *4W	0	491563.087	0	0	0	0	0	0
MgCl ₂ *6W	0	0	597446.583	597446.583	0	0	0	0
Mg(OH)Cl	9.728	0	0	0	0	0	186052.951	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	0	0.002	0	0	0	0.836
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0.164
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0.172	0	0	0
N ₂	0	0	0	0	0.828	0	0	0
CaCl ₂	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0.168	0	0	0

[0389]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔浆液	固体-1	固体-2	蒸气
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0.209	0
MgCl ₂ *W	0	0	0	0	0	1	0	0
MgCl ₂ *2W	1	0	0	0	0	0	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0
MgCl ₂ *6W	0	0	1	0.998	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0.791	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0
H ₂ O	0	0	0	1.76	0	0	0	103.182
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	9.996
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0

[0390]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔浆液	固体-1	固体-2	蒸气
O ₂	0	0	0	0	18.168	0	0	0
N ₂	0	0	0	0.001	99.799	0	0	0
CaCl ₂	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	38.427	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	16.332	0
MgCl ₂ *W	0	0	0	0	0	93.186	0	0
MgCl ₂ *2W	93.182	0	0	0	0	0	0	0
MgCl ₂ *4W	0	93.186	0	0	0	0	0	0
MgCl ₂ *6W	0	0	93.186	93.186	0	93.186	0	0
Mg(OH)Cl	0.004	0	0	0	0	0	76.854	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0

[0391] 实施例 3- 镁离子催化的使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的制程模拟。

[0392] 所定义参数部分包括图 7 所示的流程图。模拟结果表明,可有效地在两个单独脱

水反应（各自在其独立的室中）中加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 流以形成 $\text{Mg}(\text{OH})\text{Cl}$ ，随后进行分解反应（也在其独立的室中），从而形成 $\text{Mg}(\text{OH})\text{Cl}$ 和 HCl ，即总共三个室。使 $\text{Mg}(\text{OH})\text{Cl}$ 与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ，将其自流中滤出。将最终形成的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 再循环至第一反应器以再次开始制程。此制程并不限于用于 CaCl_2 的任一特定源。例如，其可通过使硅酸钙与 HCl 反应以得到 CaCl_2 来获得。

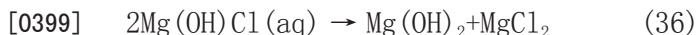
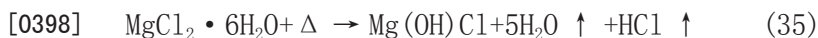
[0393] 指定用于此模拟的限制和参数包括：

[0394] • 反应是以 100% 效率运行且并无损失。在试运行测定反应效率时，可修改模拟。

[0395] • 模拟并不考虑 CaCl_2 原料或所需的任一补充 MgCl_2 （因来自系统的损失）中的杂质。

[0396] 此模拟结果表明，初步净能量消耗为 4862kwh/吨 CO_2 。表 4 提供关于模拟制程的各种流的质量和能量。每一流对应于图 7 中的流。

[0397] 制程由两个主要反应器和一个固体过滤区段组成。第一反应器加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以使其分解成 $\text{HCl}/\text{H}_2\text{O}$ 蒸汽流和 $\text{Mg}(\text{OH})\text{Cl}$ 固体流。将 $\text{HCl}/\text{H}_2\text{O}$ 蒸汽流输送至热交换器以回收额外的热。将自 $\text{Mg}(\text{OH})\text{Cl}$ 形成的 $\text{Mg}(\text{OH})_2$ 输送至反应器 2 以用于进一步处理。在此反应器中发生的化学反应包括如下：



[0400] 将 CaCl_2 溶液和烟道气流添加至反应器 2 中的 $\text{Mg}(\text{OH})_2$ 中。此反应形成 CaCO_3 、 MgCl_2 和水。 CaCO_3 发生沉淀且在过滤器或倾析器中移除。将剩余 MgCl_2 和水再循环至第一反应器中。添加额外的水以完成第一反应器所需的水平衡。在此反应器中发生的化学反应包括如下：



[0402] 此制程的主要进料是 CaCl_2 、烟道气（ CO_2 ）和水。使用、再形成且再循环系统中的 MgCl_2 。仅使用所需补充 MgCl_2 来代替与 CaCO_3 产物一起离开系统的少量 MgCl_2 和与 $\text{HCl}/\text{水}$ 产物一起离开的少量 MgCl_2 。

[0403] 此制程消耗净能量。研究能量的量并优化。存在交叉热交换以回收高温流中的热，从而预加热进料流。

[0404] 用于此制程（范例 2）的步骤汇总于下文中：

[0405]

范例 2**2 步骤脱水，然后分解**

在 2 个单独室中使六水合物脱水。步骤 1 为从六水合物到四水合物，步骤 2 为从四水合物到二水合物。二水合物分解成 100% Mg(OH)Cl。

吸收的 CO ₂	53333	MTPY
CaCl ₂	134574	MTPY
无水 HCl	88368	MTPY
CaCO ₃	105989	MTPY
再循环的六水合物	492737	MTPY
六水合物到四水合物(100 °C)	1445 kWh/吨 CO ₂	
四水合物到二水合物(125 °C)	1774 kWh/吨 CO ₂	
二水合物		
脱水和分解	1790 kWh/吨 CO ₂	
成 100% Mg(OH)Cl (130 °C)		
得到 66% HCl 蒸气		
无载体 MgCl ₂ = 较好的总效率		
不使用 HCl PP		
	0.9	
从 28% HCl 蒸气回收热	148 kWh/吨 CO ₂	
总计	4862 kWh/吨 CO₂	

[0406]

表 4a. 关于范例 2 模拟的质量和能量。

制程流名称→	5	7	8	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl 蒸气
温度 °C	98	114.1	101	25	95	40	25	100	125	130
压强 psia	14.696	14.696	14.696	14.7	14.7	15.78	14.7	14.696	22.044	14.696
质量蒸气分率	0	0	1	0	0	1	0	1	1	1
质量固体分率	1	1	0	1	1	0	0	0	0	0
质量流速 吨/年	492736.693	405410.587	306683.742	134573.943	121369.558	166332.6	234646.828	7326.106	87329.947	132027.689
体积流速 gal/min	96.405	32.909	224394.519	30.929	22.514	63660.018	6546.44	74598.258	53065.241	80593.954
焓 MW	-190.292	-144.291	-98.931	-30.599	-46.174	-17.821	-118.063	-36.806	-36.675	-25.187
密度 lb/cuft	160.371	386.542	0.043	136.522	169.146	0.082	1.125	0.037	0.052	0.051
H ₂ O	0	0	218315.265	0	0	6499.971	234646.828	7326.106	87326.106	43663.053
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0
HCl	0	0	88368.477	0	0	0	0	0	3.841	88364.636
CO ₂	0	0	0	0	0	53333.098	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18333.252	0	0	0	0
N ₂	0	0	0	0	0	88166.278	0	0	0	0

[0407]

制程流名称→	5	7	8	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl 蒸气
CaCl ₂	0	0	0	134573.943	80.499	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	121289.059	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	405410.587	0	0	0	0	0	0	0	0
MgCl ₂ *6W	492736.693	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.712	0	0	0.039	1	1	1	0.331
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0

[0408]

制程流名称→	5	7	8	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl 蒸气
HCl	0	0	0.288	0	0	0	0	0	0	0.669
CO ₂	0	0	0	0	0	0.321	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	0.11	0	0	0	0
N ₂	0	0	0	0	0	0.53	0	0	0	0
CaCl ₂	0	0	0	1	0.001	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0.999	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0	0	0
MgCl ₂ *6W	1	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0

[0409]

制程流名称→	5	7	8	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl 蒸气
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	384.27	0	0	11.441	413.016	153.708	153.708	76.854
H ₂	0	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0	0
HCl	0	0	76.854	0	0	0	0	0	0.003	76.851
CO ₂	0	0	0	0	0	38.427	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18.168	0	0	0	0
N ₂	0	0	0	0	0	99.8	0	0	0	0
CaCl ₂	0	0	0	38.45	0.023	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	38.427	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0

[0410]

制程流名称→	5	7	8	CaCl ₂	CaCO ₃	烟道气	H ₂ O	H ₂ O-1	H ₂ O-2	HCl 蒸气
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	76.854	0	0	0	0	0	0	0	0
MgCl ₂ *6W	76.854	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0

表 4b. 关于范例 2 模拟的质量和能量。

制程流名称→	液体	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔	浆液	固体-1	固体-2	蒸气
温度 °C	94.9	100	75	95	95	95	125	130	118.1
压强 psia	14.696	14.696	14.696	14.7	14.7	14.7	22.044	14.696	14.696
质量蒸气分率	0.979	0	0	0	1	0	0	0	1
质量固体分率	0	1	1	0.998	0	0.998	1	1	0
质量流速 吨/年	306683.742	405410.587	492736.693	493737.578	106499.178	615107.136	318080.64	186052.951	306683.742
体积流速 gal/min	215496.035	32.909	96.405	126.575	56469.408	146.834	32.909	32.909	234621.606
焓 MW	-99.487	-144.553	-190.849	-190.859	0.241	-237.034	-97.128	-61.083	-98.668

[0411]

制程流名称→	液体	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔	浆液	固体-1	固体-2	蒸气
密度 lb/cuft	0.045	386.542	160.371	122.394	0.059	131.442	303.277	177.393	0.041
H ₂ O	218315.265	0	0	1000	0	1000	0	0	218315.265
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	88368.477	0	0	0	0	0	0	0	88368.477
CO ₂	0	0	0	0	0.532	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0.165	18333.088	0.165	0	0	0
N ₂	0	0	0	0.72	88165.558	0.72	0	0	0
CaCl ₂	0	0	0	0	0	80.499	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	121289.059	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	318077.568	0	0

[0412]

制程流名称→	液体	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔	浆液	固体-1	固体-2	蒸气
MgCl ₂ *4W	0	405410.587	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	492736.693	492736.693	0	492736.693	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	186052.951	0
Mg(OH) ₂	0	0	0	0	0	0	3.072	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0
质量分率									
H ₂ O	0.712	0	0	0.002	0	0.002	0	0	0.712
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0.288	0	0	0	0	0	0	0	0.288
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0.172	0	0	0	0
N ₂	0	0	0	0	0.828	0	0	0	0
CaCl ₂	0	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0

[0413]

制程流名称→	液体	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔	浆液	固体-1	固体-2	蒸气
CaCO ₃	0	0	0	0	0	0.197	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	1	0	0
MgCl ₂ *4W	0	1	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	1	0.998	0	0.801	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	1	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0
H ₂ O	384.27	0	0	1.76	0	1.76	0	0	384.27
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	76.854	0	0	0	0	0	0	0	76.854
CO ₂	0	0	0	0	0	0	0	0	0

[0414]

制程流名称→	液体	MgCl ₂ -4W	MgCl ₂ -6W	再循环 1	RX2-通气孔	浆液	固体-1	固体-2	蒸气
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	18.168	0	0	0	0
N ₂	0	0	0	0.001	99.799	0.001	0	0	0
CaCl ₂	0	0	0	0	0	0.023	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	38.427	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	76.852	0	0
MgCl ₂ *4W	0	76.854	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	76.854	76.854	0	76.854	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	76.854	0
Mg(OH) ₂	0	0	0	0	0	0	0.002	0	0
MgO	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0

[0415] 实施例 4- 镁离子催化的使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的制程模拟。

[0416] 所定义参数部分包括图 8 中所示的流程图。模拟结果表明,可有效地在单一室

中加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 流以形成 MgO 。使 MgO 与 H_2O 反应以形成 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ，将其自流中滤出。将最终形成的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 再循环至第一反应器中以再次开始制程。此制程并不限于用于 CaCl_2 的任一特定源。例如，其可通过使硅酸钙与 HCl 反应以得到 CaCl_2 来获得。

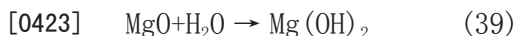
[0417] 指定用于此模拟的限制和参数包括：

[0418] • 反应是以 100% 效率运行且并无损失。在试运行测定反应效率时，可修改模拟。

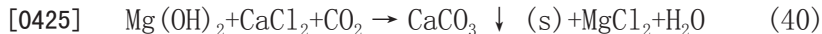
[0419] • 模拟并不考虑 CaCl_2 原料或所需的任一补充 MgCl_2 （因来自系统的损失）中的杂质。

[0420] 此模拟结果表明，初步净能量消耗为 3285kwh/ 吨 CO_2 。表 5 提供关于模拟制程的各种流的质量和能量。每一流对应于图 8 的流。

[0421] 制程由两个主要反应器和一个固体过滤区段组成。第一反应器加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以使其分解成 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流和 MgO 固体流。将 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流输送至热交换器以回收额外的热。将自 MgO 形成的 $\text{Mg}(\text{OH})_2$ 输送至反应器 2 以用于进一步处理。在此反应器中发生的化学反应包括如下：



[0424] 将 CaCl_2 溶液和烟道气流添加至反应器 2 中的 $\text{Mg}(\text{OH})_2$ 中。此反应形成 CaCO_3 、 MgCl_2 和水。 CaCO_3 发生沉淀且在过滤器或倾析器中移除。将剩余 MgCl_2 和水再循环至第一反应器中。添加额外的水以完成第一反应器所需的水平衡。在此反应器中发生的化学反应包括如下：



[0426] 此制程的主要进料是 CaCl_2 、烟道气 (CO_2) 和水。使用、再形成且再循环系统中的 MgCl_2 。仅使用所需补充 MgCl_2 来代替与 CaCO_3 产物一起离开系统的少量 MgCl_2 和与 $\text{HCl}/$ 水产物一起离开的少量 MgCl_2 。

[0427] 此制程消耗净能量。研究能量的量并优化。存在交叉热交换以回收高温流中的热，从而预加热进料流。

[0428] 用于此制程（范例 3）的步骤汇总于下文中：

[0429]

范例 3		
组合脱水/分解以得到 MgO		
使六水合物在 450° C 下同时脱水和分解。反应器得到 100%MgO。		
吸收的 CO ₂	53333	MTPY
CaCl ₂	134574	MTPY
无水 HCl	88368	MTPY
CaCO ₃	105989	MTPY
再循环的六水合物	246368	MTPY
六水合物		
脱水和分解	3778	kWh/吨 CO2
成 100% MgO (450 °C)		
得到 44.7% HCl 蒸气		
再循环一半的六水合物		
但需要高品质热		
从 45% HCl 蒸气回收热	493	kWh/吨 CO2
总计	3285	kWh/吨 CO2

[0430]

表 5a. 关于范例 3 模拟的质量和能量。

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HCl 蒸气	MgCl ₂	MgCl ₂ -6W
温度 °C	25	95	104	25	120	353.8	104
压强 psia	14.7	14.7	15.78	14.7	14.696	14.7	14.7
质量蒸气分率	0	0	1	0	1	0	0
质量固体分率	1	1	0	0	0	1	1
质量流速 吨/年	134573.943	121369.558	166332.6	125489.188	197526.11	246368.347	246368.347
体积流速 gal/min	30.929	22.514	76673.298	3501.038	137543.974	48.203	48.203
焓 MW	-30.599	-46.174	-17.479	-63.14	-52.762	-92.049	-95.073
密度 lb/cuft	136.522	169.146	0.068	1.125	0.045	160.371	160.371
H ₂ O	0	0	6499.971	125489.188	109157.633	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	88368.477	0	0
CO ₂	0	0	53333.098	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0

[0431]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HCl 蒸气	MgCl ₂	MgCl ₂ -6W
CaCl ₂	134573.943	80.499	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	246368.347	246368.347
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	0.553	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	0.447	0	0

[0432]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HCl 蒸气	MgCl ₂	MgCl ₂ -6W
CO ₂	0	0	0.321	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0
N ₂	0	0	0.53	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	1	1
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0

[0433]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HCl 蒸气	MgCl ₂	MgCl ₂ -6W
H ₂ O	0	0	11.441	220.881	192.135	0	0
H ₂	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0
HCl	0	0	0	0	76.854	0	0
CO ₂	0	0	38.427	0	0	0	0
CO	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0
N ₂	0	0	99.8	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0

[0434]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HCl 蒸气	MgCl ₂	MgCl ₂ -6W
MgCl ₂ *6W	0	0	0	0	0	38.427	38.427
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0

表 5b. 关于范例 3 模拟的质量和能量。

制程流名称→	Mg(OH)Cl	Mg(OH)Cl2	再循环 1	再循环 2	再循环 3	RX2-通气孔	浆液	蒸气	通气孔
温度 °C	450	100	95	140	140	95	95	450	140
压强 psia	14.696	14.696	14.7	14.7	14.7	14.7	14.7	14.696	14.7
质量蒸气分率	0	0	0	0.004	0	1	0	1	1
质量固体分率	1	1	0.996	0.996	1	0	0.997	0	0
质量流速 吨/年	48842.237	48842.237	247369.231	247369.231	246368.347	106499.178	368738.79	197526.11	1000.885
体积流速 gal/min	6.851	6.851	78.372	994.232	48.203	56469.408	98.632	252994.849	946.03
焓 MW	-22.38	-23	-95.676	-95.057	-94.638	0.241	-141.851	-49.738	-0.419
密度 lb/cuft	223.695	223.695	99.036	7.807	160.371	0.059	117.304	0.024	0.033
H ₂ O	0	0	1000	1000	0	0	1000	109157.633	1000
H ₂	0	0	0	0	0	0	0	0	0

[0435]

制程流名称→	Mg(OH)Cl	Mg(OH)Cl ₂	再循环 1	再循环 2	再循环 3	RX2-通气孔	浆液	蒸气	通气孔
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	88368.477	0
CO ₂	0	0	0	0	0	0.532	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0.165	0.165	0	18333.088	0.165	0	0.165
N ₂	0	0	0.72	0.72	0	88165.558	0.72	0	0.72
CaCl ₂	0	0	0	0	0	0	80.499	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	121289.059	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	246368.347	246368.347	246368.347	0	246368.347	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0

[0436]

制程流名称→	Mg(OH)ClI	Mg(OH)Cl2	再循环 1	再循环 2	再循环 3	RX2-通气孔	浆液	蒸气	通气孔
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	48842.237	48842.237	0	0	0	0	0	0	0
H ₂ O	0	0	0.004	0.004	0	0	0.003	0.553	0.999
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	0.447	0
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	0.172	0	0	0
N ₂	0	0	0	0	0	0.828	0	0	0.001
CaCl ₂	0	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	0.329	0	0
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0

[0437]

制程流名称→	Mg(OH)Cl	Mg(OH)Cl ₂	再循环 1	再循环 2	再循环 3	RX2-通气孔	浆液	蒸气	通气孔
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0.996	0.996	1	0	0.668	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	1	1	0	0	0	0	0	0	0
H ₂ O	0	0	1.76	1.76	0	0	1.76	192.135	1.76
H ₂	0	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0	76.854	0
CO ₂	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	18.168	0	0	0
N ₂	0	0	0.001	0.001	0	99.799	0.001	0	0.001
CaCl ₂	0	0	0	0	0	0	0.023	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0	38.427	0	0

[0438]

制程流名称→	Mg(OH)Cl	Mg(OH)Cl2	再循环 1	再循环 2	再循环 3	RX2-通气孔	浆液	蒸气	通气孔
MgCO ₃	0	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	38.427	38.427	38.427	0	38.427	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0
MgO	38.427	38.427	0	0	0	0	0	0	0

[0439] 实施例 5- 镁离子催化的使用 CaCl₂ 从烟道气捕获 CO₂ 以形成 CaCO₃ 的制程模拟。

[0440] 所定义参数部分包括图 9 中所示的流程图。模拟结果表明,可有效地在单一室中

加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 流以形成 $\text{Mg}(\text{OH})\text{Cl}$ 。使 $\text{Mg}(\text{OH})\text{Cl}$ 与 H_2O 反应以形成 MgCl_2 和 $\text{Mg}(\text{OH})_2$ ， $\text{Mg}(\text{OH})_2$ 随后与饱和 $\text{CaCl}_2/\text{H}_2\text{O}$ 溶液和来自烟道气的 CO_2 反应以形成 CaCO_3 ，将其自流中滤出。将最终形成的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 再循环至第一反应器中以再次开始制程。此制程并不限于用于 CaCl_2 的任一特定源。例如，其可通过使硅酸钙与 HCl 反应以得到 CaCl_2 来获得。

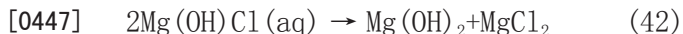
[0441] 指定用于此模拟的限制和参数包括：

[0442] • 反应是以 100% 效率运行且并无损失。在试运行测定反应效率时，可修改模拟。

[0443] • 模拟并不考虑 CaCl_2 原料或所需的任一补充 MgCl_2 （因来自系统的损失）中的杂质。

[0444] 此模拟结果表明，初步净能量消耗为 4681kwh/ 吨 CO_2 。表 6 提供关于模拟制程的各种流的质量和能量。每一流对应于图 9 的流。

[0445] 制程由两个主要反应器和一个固体过滤区段组成。第一反应器加热 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 以使其分解成 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流和 $\text{Mg}(\text{OH})\text{Cl}$ 固体流。将 $\text{HCl}/\text{H}_2\text{O}$ 蒸气流输送至热交换器以回收额外的热。将自 $\text{Mg}(\text{OH})\text{Cl}$ 形成的 $\text{Mg}(\text{OH})_2$ 输送至反应器 2 以用于进一步处理。在此反应器中发生的化学反应包括如下：



[0448] 将 CaCl_2 溶液和烟道气流添加至反应器 2 中的 $\text{Mg}(\text{OH})_2$ 中。此反应形成 CaCO_3 、 MgCl_2 和水。 CaCO_3 发生沉淀且在过滤器或倾析器中移除。将剩余 MgCl_2 和水再循环至第一反应器中。添加额外的水以完成第一反应器所需的水平衡。在此反应器中发生的化学反应包括如下：



[0450] 此制程的主要进料是 CaCl_2 、烟道气（ CO_2 ）和水。使用、再形成且再循环系统中的 MgCl_2 。仅使用所需补充 MgCl_2 来代替与 CaCO_3 产物一起离开系统的少量 MgCl_2 和与 $\text{HCl}/$ 水产物一起离开的少量 MgCl_2 。

[0451] 此制程消耗净能量。研究能量的量并优化。存在交叉热交换以回收高温流中的热，从而预加热进料流。

[0452] 用于此制程（范例 4）的步骤汇总于下文中：

[0453]

范例 4**组合脱水/分解成 $\text{Mg}(\text{OH})\text{Cl}$**

使六水合物在 250°C 同时脱水和分解。反应器得到 100% $\text{Mg}(\text{OH})\text{Cl}$ 。

吸收的 CO_2	53333	MTPY
CaCl_2	134574	MTPY
无水 HCl	88368	MTPY
CaCO_3	105989	MTPY
再循环的六水合物	492737	MTPY
脱水和分解	5043	kWh/吨 CO_2
成 100% $\text{Mg}(\text{OH})\text{Cl}$ (250°C)		
得到 28.8% HCl 蒸气		
	2.2	MW
回收热	361	kWh/吨 CO_2
从 28% HCl 蒸气		
总计	4681	kWh/吨 CO_2

[0454]

表 6a. 关于范例 4 模拟的质量和能量。

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)ClH
温度 °C	25	95	104	25	120	188	104	250
压强 psia	14.7	14.7	15.78	14.7	14.696	14.7	14.7	14.696
质量蒸气分率	0	0	1	0	1	0	0	0
质量固体分率	1	1	0	0	0	1	1	1
质量流速 吨/年	134573.943	121369.558	166332.6	234646.82	306683.742	492736.693	492736.693	186052.951
体积流速 gal/min	30.929	22.514	76673.298	6546.44	235789.67	96.405	96.405	32.909
焓 MW	-30.599	-46.174	-17.479	-118.063	-98.638	-188.114	-190.147	-60.661
密度 lb/cuft	136.522	169.146	0.068	1.125	0.041	160.371	160.371	177.393
H ₂ O	0	0	6499.971	234646.82	218315.265	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	88368.477	0	0	0
CO ₂	0	0	53333.098	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18333.252	0	0	0	0	0
N ₂	0	0	88166.278	0	0	0	0	0

[0455]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl
CaCl ₂	134573.943	80.499	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	121289.059	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	492736.693	492736.693	0
Mg(OH)Cl	0	0	0	0	0	0	0	186052.951
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	0	0.039	1	0.712	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0.288	0	0	0

[0456]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl
CO ₂	0	0	0.321	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0.11	0	0	0	0	0
N ₂	0	0	0.53	0	0	0	0	0
CaCl ₂	1	0.001	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0.999	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	1	1	0
Mg(OH)Cl	0	0	0	0	0	0	0	1
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0

[0457]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl
H ₂ O	0	0	11.441	413.016	384.27	0	0	0
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	76.854	0	0	0
CO ₂	0	0	38.427	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	18.168	0	0	0	0	0
N ₂	0	0	99.8	0	0	0	0	0
CaCl ₂	38.45	0.023	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	38.427	0	0	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0

[0458]

制程流名称→	CaCl ₂	CaCO ₃	烟道气	H ₂ O	HClVAP	MgCl ₂	MgCl ₂ -6W	Mg(OH)Cl
MgCl ₂ *6W	0	0	0	0	0	76.854	76.854	0
Mg(OH)Cl	0	0	0	0	0	0	0	76.854
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0

表 6b. 关于范例 4 模拟的质量和能量。

制程流名称→	Mg(OH)Cl ₂	再循环1	再循环2	再循环3	RX2-通气孔	浆液	蒸气	通气孔
温度 °C	100	95	113.8	113.8	95	95	250	113.8
压强 psia	14.696	14.7	14.7	14.7	14.7	14.7	14.696	14.7
质量蒸气分率	0	0	0.002	0	1	0	1	1
质量固体分率	1	0.998	0.998	1	0	0.998	0	0
质量流速 吨/年	186052.95	493737.58	493737.58	492736.69	106499.18	615107.14	306683.74	1000.89
体积流速 gal/min	32.909	126.575	982.405	96.405	56469.408	146.834	313756.5	886
焓 MW	-61.189	-190.859	-190.331	-189.91	0.241	-237.034	-96.605	-0.421
密度 lb/cuft	177.393	122.394	15.769	160.371	0.059	131.442	0.031	0.035
H ₂ O	0	1000	1000	0	0	1000	218315.27	1000
H ₂	0	0	0	0	0	0	0	0

[0459]

制程流名称→	Mg(OH)Cl ₂	再循环1	再循环2	再循环3	RX2-通气孔	浆液	蒸气	通气孔
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	88368.477	0
CO ₂	0	0	0	0	0.532	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0.165	0.165	0	18333.088	0.165	0	0.165
N ₂	0	0.72	0.72	0	88165.558	0.72	0	0.72
CaCl ₂	0	0	0	0	0	80.499	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	121289.06	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	492736.69	492736.69	492736.69	0	492736.69	0	0
Mg(OH)Cl	186052.95	0	0	0	0	0	0	0

[0460]

制程流名称→	Mg(OH)Cl ₂	再循环1	再循环2	再循环3	RX2-通气孔	浆液	蒸气	通气孔
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	0.002	0.002	0	0	0.002	0.712	0.999
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	0.288	0
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0.172	0	0	0
N ₂	0	0	0	0	0.828	0	0	0.001
CaCl ₂	0	0	0	0	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	0.197	0	0
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0

[0461]

制程流名称→	Mg(OH)Cl ₂	再循环1	再循环2	再循环3	RX2-通气孔	浆液	蒸气	通气孔
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0.998	0.998	1	0	0.801	0	0
Mg(OH)Cl	1	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0
H ₂ O	0	1.76	1.76	0	0	1.76	384.27	1.76
H ₂	0	0	0	0	0	0	0	0
Cl ₂	0	0	0	0	0	0	0	0
HCl	0	0	0	0	0	0	76.854	0
CO ₂	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	18.168	0	0	0
N ₂	0	0.001	0.001	0	99.799	0.001	0	0.001
CaCl ₂	0	0	0	0	0	0.023	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0
CaCO ₃	0	0	0	0	0	38.427	0	0

[0462]

制程流名称→	Mg(OH)Cl ₂	再循环1	再循环2	再循环3	RX2-通气孔	浆液	蒸气	通气孔
MgCO ₃	0	0	0	0	0	0	0	0
Ca(O)Cl ₂	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	76.854	76.854	76.854	0	76.854	0	0
Mg(OH)Cl	76.854	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0

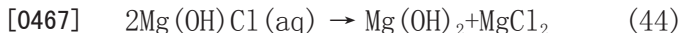
[0463] 实施例 6- 道路用盐锅炉 :MgCl₂ • 6H₂O 的分解

[0464] 图 10 示出 MgCl₂ • 6H₂O 的经加热样品的质量百分比的图表。样品初始质量为大

约 70mg 且设定为 100%。在实验期间,在样品热分解的同时测量其质量。使温度迅速斜升至 150℃,且然后以 0.5℃ / 分钟缓慢升高。在大约 220℃,重量变得恒定,这与形成 Mg(OH)Cl 一致。不存在进一步重量降低表明几乎所有的水均已被去除。两种不同的详细分解质量分析示于图 28 和 29 中,其中示出不同最终材料的理论稳态。图 30 确认 MgO 可通过比产生 Mg(OH)Cl 的温度更高的温度(此处为 500℃)制得。

[0465] 实施例 7 - Mg(OH)Cl 在 H₂O 中的溶解

[0466] 将通过 MgCl₂·6H₂O 的加热分解所产生的 Mg(OH)Cl 样品溶于水中并搅拌一定时间段。然后,干燥剩余沉淀,收集并分析。通过分解式,可对 Mg(OH)₂ 的量与预期量进行比较并分析。化学反应可表示如下:



[0468] Mg(OH)₂ 和 MgCl₂ 的溶解度数据如下:

[0469] MgCl₂ 52.8gm 于 100gm. H₂O 中(极易溶解)

[0470] Mg(OH)₂ 0.0009gm 于 100gm. H₂O 中(实际上不溶)

[0471] 所回收 Mg(OH)₂ 的理论重量:

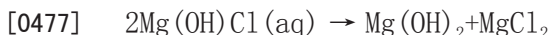
[0472] 样品的给定重量:3.0136gm。

[0473] MW Mg(OH)Cl 76.764

[0474] MW Mg(OH)₂ 58.32

[0475] 每摩尔 Mg(OH)Cl 所形成的 Mg(OH)₂ 摩尔数 = 1/2

[0476] Mg(OH)₂ 的预期量



[0478] $3.016\text{gm} * (\text{MW Mg}(\text{OH})_2 \div (\text{MW Mg}(\text{OH})\text{Cl} * 1/2)) = 1.1447\text{gm}$

[0479] 所收集沉淀物 = 1.1245gm

[0480] 理论收集% = $(1.1447 \div 1.1245) * 100 = 98.24\%$

[0481] 分析数据:

[0482] 接下来,将 Mg(OH)₂ 样品输送用于 XRD(X 射线衍射)和 EDS 分析。结果示于图 11 中。上行的峰是样品峰,中行的尖峰是 Mg(OH)₂ 的特征,而下部的尖峰是 MgO 的特征。因此表明,来自 Mg(OH)Cl 溶解的所回收沉淀物具有类似于 Mg(OH)₂ 的信号。

[0483]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.9472	1.014	96.88	96.02	+/- 0.23
Si-K	0.0073	2.737	1.74	1.99	+/- 0.17
Cl-K	0.0127	1.570	1.38	2.00	+/- 0.16
总计	100.00	100.00			

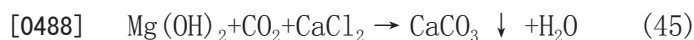
[0484] 注意:结果不包含 Z<11 的元素(Na)。

[0485] EDS 分析揭示了极少的氯 [Cl] 被并入沉淀中。注意,此分析不能检测氧或氢。

[0486] 实施例 8- 去二氧化碳起泡实验:通过使 CO₂ 与 Mg(OH)₂(或 Mg(OH)Cl) 和 CaCl₂ 反

应产生 CaCO_3

[0487] 将大约 20 克 $\text{Mg}(\text{OH})_2$ 以及两升水置于起泡柱中且通过其使 CO_2 鼓泡达 x 分钟的时间段。然后,收集一些液体,向其中添加 CaCl_2 溶液。立即形成沉淀物且将其输送用于 XRD 和 EDS。化学反应可如下表示:



[0489] XRD 分析(图 12)与 CaCO_3 特征相吻合。

[0490] EDS

[0491]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt% Err.
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[0492]

Mg-K	0.0070	2.211	2.52	1.55	+/- 0.10
Al-K	0.0013	1.750	0.33	0.22	+/- 0.04
Si-K	0.0006	1.382	0.12	0.09	+/- 0.03
Cl-K	0.0033	1.027	0.38	0.34	+/- 0.03
Ca-K	0.9731	1.005	96.64	97.80	+/- 0.30
总计	100.00	100.00			

[0493] 注意:结果不包含 $Z < 11$ 的元素(Na)。

[0494] EDS 分析表明 CaCO_3 几乎是纯的且仅具有 1.55 重量%镁杂质且几乎没有来自 CaCl_2 的氯。

[0495] 实施相同测试,但使用来自 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 分解的 $\text{Mg}(\text{OH})\text{Cl}$ 代替 $\text{Mg}(\text{OH})_2$ 。尽管 $\text{Mg}(\text{OH})\text{Cl}$ 所具有的氢氧根 $[\text{OH}^-]$ 为 $\text{Mg}(\text{OH})_2$ 的一半,但预计可吸收 CO_2 且形成沉淀 CaCO_3 (PCC)。

[0496] XRD 分析(图 13)与 CaCO_3 特征相吻合。

[0497] EDS

[0498] $\text{Chi-sqd} = 5.83$, 活时间 = 300.0Sec。

[0499] 无标分析

[0500] PROZA 校正加速电压 = 20kV, 出射角 = 35.00 度重复数 = 3

[0501]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.0041	2.224	1.48	0.90	+/- 0.09
S -K	0.0011	1.071	0.14	0.11	+/- 0.04
Ca-K	0.9874	1.003	98.38	98.98	+/- 0.34
总计	100.00	100.00			

[0502] 注意 :结果不包含 Z<11 的元素 (Na)。

[0503] 同样,结果表明 CaCO_3 几乎是纯的且几乎没有 Mg 或 Cl 化合物。实施例 9A - 岩石熔化器实验 :橄榄石和蛇纹石与 HCl 的反应

[0504] 将橄榄石 $(\text{Mg, Fe})_2\text{SiO}_4$ 和蛇纹石 $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ 的样品粉碎且使其与 6.1 摩尔 HCl 经大约 72 小时的时段发生反应。运行两组测试,第一组在室温下且第二组在 70℃ 下。这些矿物质具有可变通式且通常含有铁。在过滤样品之后,将所得滤出物 (filtrand) 和滤液在烘箱中干燥过夜。然后将样品进行 XRD 和 EDS 分析。滤液应存在 MgCl_2 且滤出物应主要是 SiO_2 。

[0505] 橄榄石滤液与 HCl 在室温下发生反应

[0506]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1960	1.451	37.06	28.45	+/- 0.18
Si-K	0.0103	1.512	1.75	1.56	+/- 0.11
Cl-K	0.5643	1.169	58.89	65.94	+/- 0.31
Fe-K	0.0350	1.161	2.30	4.06	+/- 0.22
总计	100.00	100.00			

[0507] 橄榄石滤液与 HCl 在 70℃ 下发生反应

[0508] 注意 :结果不包含 Z<11 的元素 (Na)。

[0509]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1172	1.684	27.39	19.74	+/- 0.12
Si-K	0.0101	1.459	1.77	1.48	+/- 0.07
Cl-K	0.5864	1.142	63.70	66.94	+/- 0.24
Fe-K	0.0990	1.144	6.84	11.33	+/- 0.21
Ni-K	0.0045	1.128	0.29	0.51	+/- 0.09
总计	100.00	100.00			

[0510] 蛇纹石滤液与 HCl 在室温下发生反应

[0511] 注意 :结果不包含 Z<11 的元素 (Na)。

[0512]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1674	1.466	32.47	24.53	+/- 0.15

[0513]

Al-K	0.0025	1.863	0.55	0.46	+/- 0.06
Si-K	0.0033	1.456	0.55	0.48	+/- 0.04
Cl-K	0.6203	1.141	64.22	70.77	+/- 0.27
Ca-K	0.0016	1.334	0.17	0.21	+/- 0.05
Cr-K	0.0026	1.200	0.19	0.31	+/- 0.07
Mn-K	0.0011	1.200	0.08	0.14	+/- 0.08
Fe-K	0.0226	1.160	1.51	2.62	+/- 0.10
Ni-K	0.0042	1.128	0.26	0.48	+/- 0.10
总计	100.00	100.00			

[0514] 蛇纹石滤液与 HCl 在 70℃下发生反应

[0515] 注意 :结果不包含 Z<11 的元素 (Na)。

[0516]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1759	1.455	33.67	25.59	+/- 0.14
Al-K	0.0017	1.886	0.39	0.33	+/- 0.06
Si-K	0.0087	1.468	1.46	1.28	+/- 0.04
Cl-K	0.6014	1.152	62.46	69.27	+/- 0.25
Cr-K	0.0016	1.199	0.12	0.19	+/- 0.06
Fe-K	0.0268	1.161	1.78	3.11	+/- 0.17
Ni-K	0.0020	1.130	0.12	0.22	+/- 0.08
总计	100.00	100.00			

[0517] 注意 :结果不包含 Z<11 的元素 (Na)。

[0518] 两种矿物质蛇纹石和橄榄石在环境条件和 70℃下的滤液均清晰地表明存在 MgCl₂, 并且在橄榄石的情形下存在少量 FeCl₂。

[0519] 橄榄石滤出物与 HCl 在室温下发生反应

[0520]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
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[0521]

Mg-K	0.2239	1.431	37.68	32.04	+/- 0.14
Si-K	0.3269	1.622	53.96	53.02	+/- 0.19
Cl-K	0.0140	1.658	1.87	2.32	+/- 0.06
Cr-K	0.0090	1.160	0.58	1.05	+/- 0.08
Mn-K	0.0013	1.195	0.08	0.16	+/- 0.09
Fe-K	0.0933	1.167	5.57	10.89	+/- 0.26
Ni-K	0.0045	1.160	0.25	0.52	+/- 0.11
总计	100.00	100.00			

[0522] 注意 :结果不包含 Z<11 的元素 (Na)。

[0523] 橄榄石滤出物与 HCl 在 70℃ 下发生反应

[0524]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.2249	1.461	38.87	32.86	+/- 0.16
Si-K	0.3030	1.649	51.12	49.94	+/- 0.21
Cl-K	0.0223	1.638	2.96	3.65	+/- 0.14
Ca-K	0.0033	1.220	0.29	0.41	+/- 0.05
Cr-K	0.0066	1.158	0.42	0.76	+/- 0.08
Mn-K	0.0023	1.193	0.15	0.28	+/- 0.10
Fe-K	0.0937	1.163	5.61	10.89	+/- 0.29
Ni-K	0.0074	1.158	0.42	0.86	+/- 0.13
Cu-K	0.0029	1.211	0.16	0.35	+/- 0.16
总计	100.00	100.00			

[0525] 注意 :结果不包含 Z<11 的元素 (Na)。

[0526] 假设橄榄石的通式为 $(\text{Mg}, \text{Fe})_2\text{SiO}_4$, 且此是富镁橄榄石。原料化合物具有 2 :1 的 Mg :Si 比率。然而, 不通过过滤器的滤出物具有 (37+5.5 :52) 或 0.817 :1 的 (Mg+Fe :Si) 比率。(图表上的原子%), 显而易见, 大于 50% 的镁通过了过滤器。

[0527] 蛇纹石滤出物与 HCl 在室温下发生反应

[0528]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1930	1.595	37.32	30.78	+/- 0.15
Si-K	0.2965	1.670	51.94	49.50	+/- 0.20
Cl-K	0.0065	1.633	0.88	1.06	+/- 0.06
Cr-K	0.0056	1.130	0.36	0.63	+/- 0.08
Fe-K	0.1532	1.155	9.33	17.69	+/- 0.31
Ni-K	0.0029	1.159	0.17	0.34	+/- 0.12
总计	100.00	100.00			

[0529] 注意 :结果不包含 Z<11 的元素 (Na)。

[0530] 蛇纹石滤出物与 HCl 在 70℃ 下发生反应

[0531]

元素 (计算值)	k-比率 Wt %	ZAF (1-Sigma)	原子%	元素	Wt % Err.
Mg-K	0.1812	1.536	33.53	27.83	+/- 0.13
Si-K	0.3401	1.593	56.49	54.18	+/- 0.18
Cl-K	0.0106	1.651	1.45	1.75	+/- 0.11
Cr-K	0.0037	1.142	0.24	0.43	+/- 0.07
Mn-K	0.0009	1.188	0.05	0.10	+/- 0.08
Fe-K	0.1324	1.159	8.05	15.35	+/- 0.26
Ni-K	0.0032	1.160	0.18	0.37	+/- 0.11
总计	100.00	100.00			

[0532] 注意 :结果不包含 Z<11 的元素 (Na)。

[0533] 假设蛇纹石的通式为 $(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$, 则 (Mg+Fe) 与 Si 的初始为 1.5:1 的比率降为 $(37+9.3:56.5) = 0.898:1$ 。

[0534] 实施例 9B - $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 分解的温度 / 压强模拟

[0535] 如下文 (表 7) 和图 14 所示, 改变压强和温度以测定其对 $\text{MgCl}_2 \cdot 6(\text{H}_2\text{O})$ 分解的平衡的影响。输入物是 :

[0536] 1) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0537] 2) CaCl_2

[0538] 3) 离开热交换器 (HX) 的标记为 Mg(OH)Cl 的热流的温度 (参见图 7-8)。

[0539] 4) 在倾析器中分离的固体的百分比。

[0540] 5) 标记为 H_2O 的所需水

[0541] 6) 烟道气。

[0542] 表 7.

[0543]

变化 1	变化 2	输入	Mg(OH)Cl	MgO	Q	
反应器 1	反应器 1					
参数	参数					
温度	压力					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/ 吨 CO ₂
400	5	51.08399	25.31399	25.77001	23.63765	3883
410	5	38.427	0	38.427	19.85614	3261
420	5	38.427	0	38.427	19.87482	3264
430	5	38.427	0	38.427	19.89354	3268
440	5	38.427	0	38.427	19.9123	3271
450	5	38.427	0	38.427	19.93111	3274
400	7	76.854	76.854	0	31.37484	5153
410	7	53.24627	29.63854	23.60773	24.31186	3993
420	7	38.427	0	38.427	19.87482	3264
430	7	38.427	0	38.427	19.89354	3268
440	7	38.427	0	38.427	19.9123	3271
450	7	38.427	0	38.427	19.93111	3274
400	9	76.854	76.854	0	31.37484	5153
410	9	72.85115	68.84829	4.002853	30.20646	4961
420	9	50.2148	23.5756	26.6392	23.42411	3847

[0544]

变化 1	变化 2	输入	Mg(OH)Cl	MgO	Q	
反应器 1	反应器 1					

参数	参数					
温度	压力					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/ 吨 CO ₂
430	9	38.427	0	38.427	19.89354	3268
440	9	38.427	0	38.427	19.9123	3271
450	9	38.427	0	38.427	19.93111	3274
400	11	76.854	76.854	0	31.37484	5153
410	11	76.854	76.854	0	31.41	5159
420	11	64.78938	52.72476	12.06462	27.81251	4568
430	11	44.67748	12.50096	32.17652	21.77822	3577
440	11	38.427	0	38.427	19.9123	3271
450	11	38.427	0	38.427	19.93111	3274
400	13	76.854	76.854	0	31.37484	5153
410	13	76.854	76.854	0	31.41	5159
420	13	76.854	76.854	0	31.44515	5165
430	13	55.59535	34.3367	21.25865	25.07026	4118
440	13	38.427	0	38.427	19.9123	3271
450	13	38.427	0	38.427	19.93111	3274
400	15	76.854	76.854	0	31.37484	5153
410	15	76.854	76.854	0	31.41	5159
420	15	76.854	76.854	0	31.44515	5165
430	15	66.51322	56.17244	10.34078	28.36229	4659
440	15	46.41875	15.98351	30.43525	22.32544	3667
450	15	38.427	0	38.427	19.93111	3274

200	5	127	76.854	0	47.51946	7805
210	5	85	76.854	0	33.34109	5476
220	5	77	76.854	0	30.74184	5049
230	5	77	76.854	0	30.77702	5055

[0545]

变化 1	变化 2	输入	Mg(OH)Cl	MgO	Q	
反应器 1	反应器 1					
参数	参数					
温度	压力					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/ 吨 CO ₂
240	5	77	76.854	0	30.8122	5061
250	5	77	76.854	0	30.84739	5067
200	7	184	76.854	0	66.57309	10935
210	7	125	76.854	0	46.75184	7679
220	7	85	76.854	0	33.32609	5474
230	7	77	76.854	0	30.777	5055
240	7	77	76.854	0	30.81218	5061
250	7	77	76.854	0	30.84737	5067
200	9	297	76.854	0	89.51079	14702
210	9	165	76.854	0	60.16258	9882
220	9	113	76.854	0	42.92123	7050
230	9	78	76.854	0	31.04401	5099
240	9	77	76.854	0	30.81217	5061
250	9	77	76.854	0	30.84735	5067

200	11	473	76.854	0	136.5784	22433
210	11	205	76.854	0	73.57332	12084
220	11	142	76.854	0	52.51638	8626
230	11	98	76.854	0	38.01558	6244
240	11	77	76.854	0	30.81216	5061
250	11	77	76.854	0	30.84734	5067
200	13	684	76.854	0	192.9858	31698
210	13	303	76.854	0	91.43505	15018
220	13	170	76.854	0	62.11152	10202
230	13	119	76.854	0	44.98715	7389
240	13	83.3323	76.854	0	33.00459	5421

[0546]

变化 1	变化 2	输入	Mg(OH)Cl	MgO	Q	
反应器 1	反应器 1					
参数	参数					
温度	压力					
°C	PSIA	MOL/SEC	MOL/SEC	MOL/SEC	MW	kWh/ 吨 CO ₂
250	13	76.854	76.854	0	30.84733	5067
200	15	930.5287	76.854	0	258.7607	42502
210	15	422.9236	76.854	0	123.7223	20322
220	15	198.7291	76.854	0	71.70666	11778
230	15	139.6567	76.854	0	51.95871	8534
240	15	98.51739	76.854	0	38.14363	6265
250	15	76.854	76.854	0	30.84733	5067

[0547] 实施例 10-21

[0548] 下列其他实施例是关于使用来自煤或天然气发电厂的废热排放获得所需热来实施分解反应。为从煤烟道气排放获得所需热,热源可位于袋滤室(其中温度介于320-480℃之间)之前来替代空气预加热器。参见以下参考文献:“The structural design of air and gas ducts for power stations and industrial Boiler Applications”的第11-15页,出版商:American Society of Civil Engineers(1995年8月),其全部内容以引用方式并入本文中。开放式循环天然气发电厂具有600℃的极高排气温度。参见以下参考文献:“The structural design of air and gas ducts for power stations and industrial Boiler Applications”的第11-15页,出版商:American Society of Civil Engineers(1995年8月),其全部内容以引用方式并入本文中。另外, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 的分解反应也可以两种不同模式运行,即完全分解成MgO或部分分解成 $\text{Mg}(\text{OH})\text{Cl}$ 。部分分解成 $\text{Mg}(\text{OH})\text{Cl}$ 在一些实施方案中需要大于180℃的温度,而全部分解成MgO在一些实施方案中需要440℃或更高的温度。

[0549] 另外,制程的流入进料可表示为介于100%硅酸钙(CaSiO_3)与100%硅酸镁(MgSiO_3)之间的连续体,其中透辉石($\text{MgCa}(\text{SiO}_3)_2$)(或 CaSiO_3 和 MgSiO_3 的1:1摩尔比的混合物)表示50%的中间情形。对于这些情形中的每一个而言,所得输出物在一些实施方案中介于碳酸钙(CaCO_3)至碳酸镁(MgCO_3)之间,其中白云石 $\text{CaMg}(\text{CO}_3)_2$ 表示中间情形。使用100%硅酸钙的制程是用于所有先前建模实施方案中的Ca-Mg制程。还着重注意的是,100%硅酸镁制程不使用钙化合物;而100%硅酸钙流入进料制程使用镁化合物,但在再循环环路中,仅需要补充镁化合物。

[0550] 关于Ca-Mg、仅Mg、透辉石制程(例如,使用将水合 MgCl_2 分别完成和部分分解成MgO和 $\text{Mg}(\text{OH})\text{Cl}$)的其他细节描述于下文中。

[0551] 1)Ca-Mg制程

[0552] 总反应为 $\text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2$

[0553] a)完全分解(“ CaSiO_3 -MgO制程”):

[0554] 1) $\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \Delta \rightarrow \text{MgO} + 5\text{H}_2\text{O} \uparrow + 2\text{HCl} \uparrow$

[0555] 热分解反应。

[0556] 2) $2\text{HCl}(\text{aq}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{SiO}_2 \downarrow + \text{H}_2\text{O}$

[0557] 岩石熔融反应。

[0558] 注意:在反应期间,每2摩尔HCl存在5摩尔 H_2O 。

[0559] 3) $\text{MgO} + \text{CaCl}_2(\text{aq}) + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{MgCl}_2(\text{aq})$

[0560] 此式的一些形式(versions)使用自MgO和 H_2O 形成的 $\text{Mg}(\text{OH})_2$ 。

[0561] 4) $\text{MgCl}_2(\text{aq}) + 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0562] 再生 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$,使其返回第1步中。

[0563] b)部分分解(“ CaSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ 制程”):

[0564] 1) $2 \times [\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \Delta \rightarrow \text{Mg}(\text{OH})\text{Cl} + 5\text{H}_2\text{O} \uparrow + \text{HCl} \uparrow]$

[0565] 热分解。

[0566] 需要多达2倍的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 来捕集相同量的 CO_2 。

[0567] 2) $2\text{HCl}(\text{aq}) + \text{CaSiO}_3 \rightarrow \text{CaCl}_2(\text{aq}) + \text{SiO}_2 \downarrow + \text{H}_2\text{O}$

[0568] 岩石熔融反应。

[0569] $3) 2\text{Mg}(\text{OH})\text{Cl} + \text{CaCl}_2(\text{aq}) + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + 2\text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}$

[0570] CO_2 捕获反应

[0571] $4) 2\text{MgCl}_2 + 12\text{H}_2\text{O} \rightarrow 2\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0572] 再生 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 使其返回第 1 步中。

[0573] II) 仅 Mg 的制程

[0574] 总反应为 $\text{MgSiO}_3 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{SiO}_2$

[0575] c) 完全分解 (“ MgSiO_3 -MgO 制程”) :

[0576] $1) 2\text{HCl}(\text{aq}) + \text{MgSiO}_3 + (\text{x}-1)\text{H}_2\text{O} \rightarrow \text{MgCl}_2 + \text{SiO}_2 \downarrow + \text{xH}_2\text{O}$

[0577] 岩石熔融反应。

[0578] $2) \text{MgCl}_2 \cdot \text{xH}_2\text{O} + \Delta \rightarrow \text{MgO} + (\text{x}-1)\text{H}_2\text{O} \uparrow + 2\text{HCl} \uparrow$

[0579] 热分解反应。

[0580] 注意 : 每 2 摩尔 HCl 产生 “ $\text{x}-1$ ” 摩尔 H_2O 。

[0581] $3) \text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3$

[0582] CO_2 捕获反应。

[0583] 注意, 在此实施方案中, 无需再循环 MgCl_2 。x 值 (水合水的数量) 远小于 6, 这是因来自岩石熔融反应的 MgCl_2 足够热以驱动大量水进入蒸气相中。因此, 来自岩石熔化的路径在稳态下运行, 且如所建模的那样, “x” 具有大约为 2 的值。

[0584] d) 部分分解 (“ MgSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ 制程”) :

[0585] $1) 2\text{HCl}(\text{aq}) + \text{MgSiO}_3 \rightarrow \text{MgCl}_2 + \text{SiO}_2 \downarrow + \text{H}_2\text{O}$

[0586] 岩石熔融反应。

[0587] 注意 : 在反应期间, 每摩尔 HCl 存在 “ $\text{x}-1$ ” 摩尔 H_2O 。

[0588] $2) 2 \times [\text{MgCl}_2 \cdot \text{xH}_2\text{O} + \Delta \rightarrow \text{Mg}(\text{OH})\text{Cl} + (\text{x}-1)\text{H}_2\text{O} \uparrow + \text{HCl} \uparrow]$

[0589] 分解。

[0590] 需要多达 2 倍的 $\text{MgCl}_2 \cdot (\text{x}-1)\text{H}_2\text{O}$ 来捕集相同量的 CO_2 。

[0591] $3) 2\text{Mg}(\text{OH})\text{Cl} + \text{CO}_2 \rightarrow \text{MgCO}_3 \downarrow + \text{MgCl}_2 + \text{H}_2\text{O}$

[0592] CO_2 捕获反应。

[0593] $4) \text{MgCl}_2(\text{aq}) + 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0594] 再生 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 使其返回第 1 步中。

[0595] 注意, 在此实施方案中, 再循环一半 MgCl_2 。x 值 (水合水的数量) 略小于 6, 这是因为一半 MgCl_2 来自岩石熔融反应 (其足够热以驱动大量水进入蒸气相中) 且剩余的一半是在吸收塔中再循环的。因此, 全部量 MgCl_2 在稳态下的水合数具有大约为 4 的值, 平均介于 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 与 $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ 之间。

[0596] III) 透辉石或混合制程 :

[0597] 注意 : 透辉石是钙和镁的混合硅酸盐且白云石是钙和镁的混合碳酸盐。

[0598] 总反应 : $1/2\text{CaMg}(\text{SiO}_3)_2 + \text{CO}_2 \rightarrow 1/2\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2$

[0599] e) 完全分解 (“透辉石-MgO 制程”) :

[0600] $1) \text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \Delta \rightarrow \text{MgO} + 5\text{H}_2\text{O} \uparrow + 2\text{HCl} \uparrow$

[0601] 热分解。

[0602] $2) \text{HCl} + 1/2\text{CaMg}(\text{SiO}_3)_2 \rightarrow 1/2\text{CaCl}_2 + 1/2\text{MgSiO}_3 \downarrow + 1/2\text{SiO}_2 \downarrow + 1/2\text{H}_2\text{O}$

- [0603] 第一岩石熔融反应。
- [0604] $3) \text{HCl} + 1/2 \text{MgSiO}_3 \rightarrow 1/2 \text{MgCl}_2 + 1/2 \text{SiO}_2 \downarrow + 1/2 \text{H}_2\text{O}$
- [0605] 第二岩石熔融反应。使 MgCl_2 返回第 1 步中。
- [0606] $4) \text{MgO} + 1/2 \text{CaCl}_2 + \text{CO}_2 \rightarrow 1/2 \text{CaMg}(\text{CO}_3)_2 \downarrow + 1/2 \text{MgCl}_2$
- [0607] $5) 1/2 \text{MgCl}_2 + 3\text{H}_2\text{O} \rightarrow 1/2 \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- [0608] 再生 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 使其返回第 1 步中。
- [0609] f) 部分分解 (“透辉石-Mg(OH)Cl 制程”) :
- [0610] $1) 2 \times [\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \Delta \rightarrow \text{Mg}(\text{OH})\text{Cl} + 5\text{H}_2\text{O} \uparrow + \text{HCl} \uparrow]$
- [0611] 热分解。
- [0612] 需要多达 2 倍的 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 来捕集相同量的 CO_2 。
- [0613] $2) \text{HCl} + 1/2 \text{CaMg}(\text{SiO}_3)_2 \rightarrow 1/2 \text{CaCl}_2 + 1/2 \text{MgSiO}_3 \downarrow + 1/2 \text{SiO}_2 \downarrow + 1/2 \text{H}_2\text{O}$
- [0614] 第一岩石熔融反应。
- [0615] $3) \text{HCl} + 1/2 \text{MgSiO}_3 \rightarrow 1/2 \text{MgCl}_2 + 1/2 \text{SiO}_2 \downarrow + 1/2 \text{H}_2\text{O}$
- [0616] 第二岩石熔融反应。此处, 使 MgCl_2 返回第 1 步中。
- [0617] $4) 2\text{Mg}(\text{OH})\text{Cl} + 1/2 \text{CaCl}_2 + \text{CO}_2 \rightarrow 1/2 \text{CaMg}(\text{CO}_3)_2 \downarrow + 3/2 \text{MgCl}_2 + \text{H}_2\text{O}$
- [0618] $5) 3/2 \text{MgCl}_2 + 9\text{H}_2\text{O} \rightarrow 3/2 \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- [0619] 再生 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 使其返回第 1 步中
- [0620] 表 9. 制程简述
- [0621]

实施例	制成	烟道气来源	温度 $^{\circ}\text{C}^1$	烟道气的 $\text{CO}_2\%^2$	各制程流的具体质量和能量平衡
10	$\text{CaSiO}_3\text{-Mg}(\text{OH})\text{Cl}$	煤	320-550	7.2% - 18%	表 14
11	$\text{CaSiO}_3\text{-Mg}(\text{OH})\text{Cl}$	天然气	600	7.2% - 18%	表 14
12	$\text{CaSiO}_3\text{-MgO}$	煤	550	7.2% - 18%	表 15
13	$\text{CaSiO}_3\text{-MgO}$	天然气	600	7.2% - 18%	表 15
14	$\text{MgSiO}_3\text{-Mg}(\text{OH})\text{Cl}$	煤	320-550	7.2% - 18%	表 16
15	$\text{MgSiO}_3\text{-Mg}(\text{OH})\text{Cl}$	天然气	600	7.2% - 18%	表 16
16	$\text{MgSiO}_3\text{-MgO}$	煤	550	7.2% - 18%	表 17
17	$\text{MgSiO}_3\text{-MgO}$	天然气	600	7.2% - 18%	表 17
18	透辉石-Mg(OH)Cl	煤	320-550	7.2% - 18%	表 18
19	透辉石-Mg(OH)Cl	天然气	600	7.2% - 18%	表 18
20	透辉石-MgO	煤	550	7.2% - 18%	表 19
21	透辉石-MgO	天然气	600	7.2% - 18%	表 19

[0622] 1—320–550℃的温度范围包括分别在 320℃、360℃、400℃、440℃和 550℃下运行的模型。

[0623] 2—烟道气中 7.2%–18%的 CO₂ 百分比包括分别在 7.2%、10%、14%和 18%下运行的模型。

[0624] 硅酸钙制程：

[0625] 将 CaSiO₃–MgO 和 CaSiO₃–Mg(OH)Cl 分解制程进一步分成两个阶段，第一步骤由脱水反应组成，其中将 MgCl₂·6H₂O 转化成 MgCl₂·2H₂O+4H₂O，且在第二步骤中将 MgCl₂·2H₂O 转化成 Mg(OH)Cl+HCl+H₂O（若期望或需要部分分解）和 MgO+2HCl+H₂O（若期望或需要总分解）。图 15 描述此制程的布置。

[0626] 硅酸镁制程：

[0627] MgSiO₃–MgO 和 MgSiO₃–Mg(OH)Cl 制程由一室分解步骤组成，其中来自分解室的 HCl 与 MgSiO₃ 在岩石熔融反应器中反应，且在呈二水合物形式 MgCl₂·2H₂O 的 MgCl₂ 离开岩石熔融室而接近分解反应器（其中将其转化成 MgO 或 Mg(OH)Cl，如先前所述）时，反应的所得热离开 MgCl₂。若不使用硅酸钙，则可优选此制程。自分解排放的 HCl 与 MgSiO₃ 反应以形成额外 MgCl₂。硅酸镁制程遵循不同于钙的路径。制程始于“岩石熔融反应（HCl+硅酸盐）”，然后行进至“分解反应（MgCl₂+热）”，最后到达吸收塔。在硅酸钙制程中，所有镁化合物在分解反应与吸收反应之间循环。图 16 描述此制程的布置。

[0628] 混合硅酸镁和硅酸钙“透辉石”制程：

[0629] 透辉石–MgO 和透辉石–Mg(OH)Cl 中间制程也涉及由以下组成的两阶段分解：脱水反应 MgCl₂·6H₂O+Δ→MgCl₂·2H₂O+4H₂O，随后是分解反应 MgCl₂·2H₂O+Δ→MgO+2HCl+H₂O（完全分解）或 MgCl₂·2H₂O+Δ→Mg(OH)Cl+HCl+H₂O（部分分解）。图 17 描述此制程的布置。

[0630] 来自分解的所得 HCl 随后与透辉石 CaMg(SiO₃)₂ 在两步骤“岩石熔融反应”中反应。第一反应通过反应 2HCl+CaMg(SiO₃)₂→CaCl₂(aq)+MgSiO₃↓+SiO₂↓+H₂O 产生 CaCl₂。来自先前反应的固体随后与 HCl 第二次发生反应以通过反应 MgSiO₃+2HCl→MgCl₂+SiO₂↓+H₂O 产生 MgCl₂。将来自第一岩石熔化器的 CaCl₂ 传输至吸收塔且将来自第二岩石熔化器的 MgCl₂ 传输至分解反应器以制备 Mg(OH)Cl 或 MgO。

[0631] 反应基础：

[0632] 所有这些实施例均假设吸收来自所关注的已知燃煤工厂的参考烟道气的 50% CO₂。这使得能够在每一实施例之间进行比较。来自此工厂的烟道气的排放流速为 136,903,680 吨/年且此气体的 CO₂ 含量为 10 重量%。此 CO₂ 量是实施例 10 至 21 的基础，其中：

[0633] 烟道气中存在的 CO₂ 量/年：

[0634] 136,903,680 吨/年*10%=13,690,368 吨/年

[0635] 所吸收的 CO₂ 量/年。

[0636] 13,690,368 吨/年*50%=6,845,184 吨 CO₂/年。

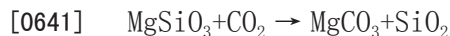
[0637] 因所吸收的 CO₂ 量是恒量，故基于反应的化学计量和每一化合物的分子量，反应物消耗和产物生成也是恒量。

[0638] 对于 CaSiO₃–MgO 和 CaSiO₃–Mg(OH)Cl 制程的所有实施例（实施例 10–13）而言，总

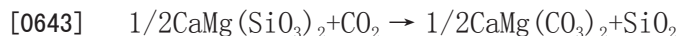
反应为：



[0640] 对于 MgSiO_3 - MgO 和 MgSiO_3 - $\text{Mg}(\text{OH})\text{Cl}$ 制程的所有实施例（实施例 14-17）而言，总反应为：



[0642] 对于透辉石- MgO 和透辉石- $\text{Mg}(\text{OH})\text{Cl}$ 制程的所有实施例（实施例 18-21）而言，总反应为：



[0644] Aspen 模型进入制程的所需输入物且计算所需烟道气以提供分解反应所需的热，从而产生吸收二氧化碳的化合物 MgO 、 $\text{Mg}(\text{OH})_2$ 或 $\text{Mg}(\text{OH})\text{Cl}$ 。此烟道气可来自天然气或煤工厂且在煤情形下在 320°C 至 550°C 的温度范围下进行测试。此烟道气不应与参考烟道气混淆，参考烟道气是用作标准来提供每一实施例所去除的具体 CO_2 量。使用较高温度烟道气的制程通常需要较少量的烟道气以从该基础 (basis) 捕获相同量的二氧化碳。另外，具有较大二氧化碳浓度的烟道气通常导致捕获二氧化碳所需的烟道气量较大，这是因需要捕获的二氧化碳量较大。

[0645] 可基于所捕获 CO_2 和用于每一实施例的每一输入物和每一输出物的分子量来确定反应物消耗和产物生成。

[0646] 表 10. 输入物和输出物的分子量（所有实施方案）。

[0647]

化合物	分子量
CaSiO_3	116.16
MgSiO_3	99.69
透辉石 *	215.85
CaCO_3	100.09
MgCO_3	84.31

[0648]

化合物	分子量
白云石 *	184.40
SiO_2	60.08
CO_2	44.01

[0649] * 必须将摩尔数除以 2 以与其他制程的 CO_2 吸收测量可比。

[0650] 对于实施例 10-13：

[0651] CaSiO_3 消耗为：

[0652] $6,845,184 \text{ 吨/年} \times (116 \cdot 16/44 \cdot 01) = 18,066,577 \text{ 吨/年}$ 。

[0653] CaCO_3 产量为：

[0654] $6,845,184 \text{ 吨/年} \times (100 \cdot 09/44 \cdot 01) = 15,559,282 \text{ 吨/年}$ 。

[0655] SiO_2 产量为：

[0656] $6,845,184 \text{ 吨/年} \times (60 \cdot 08/44 \cdot 01) = 9,344,884 \text{ 吨/年}$

[0657] 可对其他实施例进行相同类型的计算。此下表含有用于实施例 10 至 21 的输入物和输出物。基础：6,845,184 吨所吸收 CO_2 /年。

[0658] 表 11. 实施例 10-21 的输入物和输出物的质量流。

[0659]

所有测量都是以吨/年(TPY)表示			
	实施例		
	10-13	14-17	18-21
吸收的 CO_2	6,845,184	6,845,184	6,845,184
输入物			
用于 CO_2 捕获的烟道气	136,903,680	136,903,680	136,903,680
10% CO_2	13,690,368	13,690,368	13,690,368
CaSiO_3	18,066,577		
MgSiO_3		15,613,410	
透辉石			16,839,993
输出物			

[0660]

所有测量都是以吨/年(TPY)表示			
	实施例		
	10-13	14-17	18-21
SiO_2	9,344,884	9,344,884	9,344,884
CaCO_3	15,559,282		
MgCO_3		13,111,817	
白云石			14,319,845

[0661] 运行 Aspen 模型生成关于分解反应的每一步骤（脱水和分解）的下列热负荷结

果。每一实施例的结果汇总于下表中。

[0662] 表 12. 功率（各制程基于特定 CO₂ 吸收的能量等级）。

[0663]

热平衡						
制程	CaSiO ₃ -Mg(OH)Cl	CaSiO ₃ -MgO	MgSiO ₃ -Mg(OH)Cl	MgSiO ₃ -MgO	Diop.-Mg(OH)Cl	Diop.-MgO
实施例	10,11	12,13	14,15	16,17	18,19	20,21
脱水室(MW)	2670	1087	n/a	n/a	2614	1306
六水合物至二水合物(210 °C)						
源	HCl 与硅酸盐反应					
分解室(MW)	1033	1297	1226	1264	1231	1374
分解温度°C	210	450	210	450	210	450
源	烟道气					
用于 D&D*的总热(MW)	3703	2384	1226	1264	3854	2680

[0664] *D&D 等于脱水和分解

[0665]

表 13. 作为烟道气温度和 CO₂ 浓度的函数的捕获的 CO₂ 百分比。实施例 10 至 13。

制程	CaSiO ₃ -Mg(OH)Cl					CaSiO ₃ - MgO	CaSiO ₃ - Mg(OH)Cl	CaSiO ₃ - MgO
	煤 320 °C	煤 360 °C	煤 400 °C	煤 440 °C	煤 550 °C	煤 550 °C	天然气 600 °C	天然气 600 °C
烟道气来源/温度								
实施例编号	10	10	10	10	10	12	11	13
% CO ₂								
7%	33%	45%	57%	70%	105%	83%	121%	96%
10%	24%	32%	41%	50%	75%	60%	87%	69%
14%	17%	23%	29%	36%	54%	43%	62%	50%
18%	13%	18%	23%	28%	42%	33%	48%	39%

超过 100%的值表示可获得过量的热来产生更多 Mg(OH)Cl 或 MgO。图 24 说明在 CaSiO₃-Mg(OH)Cl 和 CaSiO₃-MgO 制程的实施例 10 至 13 中在以下情形下所捕获的 CO₂ 百分比：不同烟道气 CO₂ 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。

[0666]

表 14. 作为烟道气温度和 CO₂ 浓度的函数的捕获的 CO₂ 百分比。实施例 14 至 17.

制程	MgSiO ₃ -Mg(OH)Cl					MgSiO ₃ - MgO	MgSiO ₃ - Mg(OH)Cl	MgSiO ₃ - MgO
	煤 320 °C	煤 360 °C	煤 400 °C	煤 440 °C	煤 550 °C	煤 550 °C	天然气 600 °C	天然气 600 °C
烟道气来源/温度								
实施例编号	14	14	14	14	14	16	15	17
% CO ₂								
7%	24%	34%	45%	55%	84%	86%	93%	96%
10%	17%	25%	32%	40%	61%	62%	67%	69%
14%	12%	18%	23%	28%	43%	44%	48%	49%
18%	10%	14%	18%	22%	34%	34%	37%	38%

图 25 说明在 MgSiO₃-Mg(OH)Cl 和 MgSiO₃-MgO 制程的实施例 14 至 17 中在以下情形下所捕获的 CO₂ 百分比：不同烟道气 CO₂ 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。

[0668]

表 15. 作为烟道气温度和 CO₂ 浓度的函数的捕获的 CO₂ 百分比。实施例 18 至 21。

制程	透辉石-Mg(OH)Cl					Diop - MgO	Diop - Mg(OH)Cl	Diop - MgO
	煤 320 °C	煤 360 °C	煤 400 °C	煤 440 °C	煤 550 °C	煤 550 °C	天然气 600 °C	天然气 600 °C
烟道气来源/温度								
实施例编号	18	18	18	18	18	20	19	21
% CO ₂								
7%	28%	38%	48%	59%	88%	79%	101%	91%
10%	20%	27%	35%	42%	63%	57%	73%	65%
14%	14%	19%	25%	30%	45%	40%	52%	47%
18%	11%	15%	19%	23%	35%	31%	41%	36%

* 注意: Diop 等于透辉石

图 26 说明在透辉石-Mg(OH)Cl 和透辉石-MgO 制程的实施例 18 至 21 中在以下情形下所捕获的 CO₂ 百分比: 不同烟道气 CO₂ 浓度、不同温度、烟道气是源于煤或者天然气、以及制程是依赖于完全分解或者部分分解。

表 16a. 关于实施例 10 和 11 模拟的质量和能量。

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
PH										
温度 °C	112.6	95	149.9	150	95	25	100	25	200	250
压强 psia	14.696	15	100	14.696	14.7	14.696	15.78	14.7	14.696	14.696
质量蒸气分率	0	0.793	0	0	0	0	1	0	1	1
质量固体分率	1	0.207	0	0.163	1	1	0	0	0	0
质量流速 吨/年	5.73E+07	3.96E+07	4.36E+07	5.21E+07	1.41E+07	164E+07	6.21E+07	1.80E+07	3.57E+07	3.57E+07
体积流速 gal/min	11216.8	2.2E+07	17031.4	18643.542	2616.633	2126.004	3.11E+07	502184.16	3.30E+07	3.65E+07
焓 MW	-22099.5	-3288.21	-17541.7	-21585.353	-5368.73	-7309.817	-2926.806	-9056.765	-11331.898	-11240.08
密度 lb/cuft	160.371	0.059	80.305	87.619	169.173	241.725	0.063	1.125	0.034	0.031
H ₂ O	0	1.80E+07	2.79E+07	2.79E+07	0	0	3.10E+06	1.80E+07	2.54E+07	2.54E+07
HCl	0	0	0.004	0.004	0	0	0	0	1.03E+07	1.03E+07
CO ₂	0	0	0	0	0	0	6.21E+06	0	0	0
O ₂	0	0	0	0	0	0	6.21E+06	0	0	0
N ₂	0	0	0	0	0	0	4.65E+07	0	0	0
CaCO ₃	0	0	0	0	1.41E+07	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0

[0669]

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	5.73E+07	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	8.22E+06	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	3.43E+06	0	0	0	0	0	0	0	0
Ca ²⁺	0	0	5.65E+06	5.65E+06	0	0	0	0	0	0
Cl ⁻	0	1.00E+07	1.00E+07	1.00E+07	0	0	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0

[0670]

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
CaSiO ₃	0	0	0	.007	0	1.64E+07	0	0	0	0
SiO ₂	0	0	0	8.47E+06	0	0	0	0	0	0

表 16b. 关于实施例 10 和 11 模拟的质量和能量.

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 1	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
PH			9.453			9.453		
温度 C	215	80	95	95	149.9	95	250	115
压强 psia	14.696	14.696	14.7	14.7	100	14.7	14.696	14.696
质量蒸气分率	.502	0	0	1	0	0	0	.165
质量固体分率	.498	1	0	0	1	.152	1	.207
质量流速 吨/年	5.73E+07	5.73E+07	7.84E+07	5.27E+07	8.47E+06	9.26E+07	2.16E+07	3.96E+07
体积流速 gal/min	3.03E+07	11216.796	33789.492	282E+07	1607.826	32401.78	3828.933	6.33E+06
焓 MW	-1877.989	-22191.287	-32705.27	120.09	0	-38074.2	-7057.97	-4070.06
密度 lb/cuft	.059	160.371	72.846	0.059	165.327	89.628	177.393	0.197
H ₂ O	2.54E+07	0	5.16E+07	0	0	5.16E+07	0	1.80E+07
HCl	3.40E+06	0	0	0	0	0	0	0
CO ₂	0	0	0.074	25.781	0	0.074	0	0

[0671]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 I	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
O ₂	0	0	2510.379	6.20E+06	0	2510.379	0	0
N ₂	0	0	8109.244	4.65E+07	0	8109.245	0	0
CaCO ₃	0	0	0	0	0	1.41E+07	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	2.14E+07	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	5.73E+07	0	0	0	0	0	0
Mg(OH)Cl	7.15E+06	0	0	0	0	0	2.16E+07	0
Mg(OH) ₂	0	0	0	0	0	0	0	8.22E+06
MgO	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	3324.433	0	0	3324.433	0	0
SO ₂	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	6.85E+06	0	0	6.85E+06	0	3.43E+06
Ca ²⁺	0	0	1644.031	0	0	1644.031	0	0

[0672]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 1	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
Cl ⁻	0	0	2.00E+07	0	0	2.00E+07	0	1.00E+07
CO ₃	0	0	61.424	0	0	61.424	0	0
HCO ₃	0	0	27.297	0	0	27.297	0	0
OH ⁻	0	0	690.278	0	0	690.278	0	0
CaSiO ₃	0	0	0	0	0.007	0	0	0
SiO ₂	0	0	0	0	8.47E+06	0	0	0

表 17a. 关于实施例 12 和 13 模拟的质量和能量。

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
PH										
温度 °C	271	255.5	149.8	150	95	25	100	25	200	450
压强 psia	14.696	15	100	14.696	14.7	14.696	15.78	14.7	14.696	14.696
质量蒸气分率	0	0	0	0	0	0	1	0	1	1
质量固体分率	1	1	0	0.215	1	1	0	0	0	0
质量流速 吨/年	2.87E+07	2.37E+07	3.09E+07	3.94E+07	1.41E+07	1.64E+07	6.21E+07	1.80E+07	2.30E+07	2.30E+07
体积流速 gal/min	5608.398	10220.835	10147.12	11758.176	2616.827	2126.004	3.11E+07	502184.16	1.93E+07	2.94E+07
焓 MW	-10826.6	-11660.74	-11347.9	-15391.633	-5369.12	-7309.817	-2926.806	-9056.765	-6056.076	-5786.994

[0673]

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
密度 lb/cuft	160.371	72.704	95.515	105.035	169.173	241.725	0.063	1.125	0.037	0.024
H ₂ O	0	1.55E+07	1.52E+07	1.52E+07	0	0	3.10E+06	1.80E+07	1.27E+07	1.27E+07
HCl	0	0	0.015	0.015	0	0	0	0	1.03E+07	1.03E+07
CO ₂	0	0	0	0	0	0	6.21E+06	0	0	0
O ₂	0	0	0	0	0	0	6.21E+06	0	0	0
N ₂	0	0	0	0	0	0	4.65E+07	0	0	0
CaCO ₃	0	0	0	0	1.41E+07	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	2.87E+07	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	8.22E+06	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0

[0674]

制程流名称→	1	2	CaCl ₂	CaCl ₂ -Si	CaCO ₃	CaSiO ₃	烟道气	H ₂ O	HCl	HCl 蒸气
NO ₂	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	0	0	0	0	0	0	0	0
Ca ²⁺	0	0	5.65E+06	5.65E+06	0	0	0	0	0	0
Cl ⁻	0	0	1.00E+07	1.00E+07	0	0	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0.023	1.64E+07	0	0	0	0	0
SiO ₂	0	0	0	8.47E+06	0	0	0	0	0	0

表 17b. 关于实施例 12 和 13 模拟的质量和能量。

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 1	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
PH			9.304			9.304		
温度 °C	215	80	95	95	149.8	95	450	115
压强 psia	14.696	14.696	14.7	14.7	100	14.7	14.696	14.696
质量蒸气分率	0.502	0	0	1	0	0	0	0

[0675]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 1	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
质量固体分率	0.498	1	0	0	1	0.221	1	1
质量流速 吨/年	2.87E+07	2.87E+07	4.98E+07	5.27E+07	8.47E+06	6.39E+07	5.68E+06	2.37E+07
体积流速 gal/min	1.51E+07	5608.398	25330.305	2.82E+07	1607.826	22988.79	797.11	10220.84
焓 MW	-9388.949	-11095.644	-21589.89	120.08	0	-26959.3	-2603.98	-11955.9
密度 lb/cuft	0.059	160.371	61.662	0.059	165.327	87.199	223.695	72.704
H ₂ O	127E+07	0	3.63E+07	0	0	3.63E+07	0	1.55E+07
HCl	1.70E+07	0	0	0	0	0	0	0
CO ₂	0	0	0.145	79.255	0	0.145	0	0
O ₂	0	0	1919.222	6.20E+06	0	1919.222	0	0
N ₂	0	0	6199.3	4.65E+07	0	6199.301	0	0
CaCO ₃	0	0	0	0	0	1.41E+07	0	0
MgCl ₂	0	0	0	0	0	0	0	0
MgCl ₂ *W	1.07E+07	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	2.87E+07	0	0	0	0	0	0
Mg(OH)Cl	3.58E+06	0	0	0	0	0	0	0

[0676]

制程流名称→	MgCl ₂ -2W	MgCl ₂ -6W	再循环 I	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
Mg(OH) ₂	0	0	0	0	0	0	0	8.22E+06
MgO	0	0	0	0	0	0	5.68E+06	0
MgHCO ₃ ⁺	0	0	2208.676	0	0	2208.676	0	0
SO ₂	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0
Mg ²⁺	0	0	3.43E+06	0	0	3.43E+06	0	0
Ca ²⁺	0	0	1225.309	0	0	1225.309	0	0
Cl ⁻	0	0	1.00E+07	0	0	1.00E+07	0	0
CO ₃ ²⁻	0	0	110.963	0	0	110.963	0	0
HCO ₃ ⁻	0	0	63.12	0	0	63.12	0	0
OH ⁻	0	0	519.231	0	0	519.231	0	0
CaSiO ₃	0	0	0	0	0.023	0	0	0
SiO ₂	0	0	0	0	8.47E+06	0	0	0

表 18a. 关于实施例 14 和 15 模拟的质量和能量。

[0677]

制程流名称→	烟道气	H ₂ O	H ₂ O	HCl 蒸气	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
PH							
温度 °C	100	25	26	250	200.7	200	200
压强 psia	15.78	1	14.696	14.696	15	14.696	14.696
质量蒸气分率	1	0	0.798	1	0.238	0	0.169
质量固体分率	0	0	0.186	0	0	1	0.289
质量流速 吨/年	1.37E+08	1.00E+07	1.58E+08	1.69E+07	2.31E+07	4.08E+07	3.26E+07
体积流速 gal/min	62.21E+07	4569.619	4.91E+07	1.22E+07	5.22E+06	3828.933	5.33E+06
焓 MW	-5853.92	-4563.814	-13984.7	-2861.732	0	-11194.13	-10932.15
密度 lb/cuft	0.063	62.249	0.091	0.04	0.126	303.28	0.174
H ₂ O	6.85E+06	1.00E+07	5.19E+06	5.60E+06	8.37E+06	0	8.37E+06
HCl	0	0	0	1.13E+07	126399.9	0	126399.87
CO ₂	1.37E+07	0	6.85E+06	0	0	0	0
O ₂	1.37E+07	0	1.37E+07	0	0	0	0
N ₂	1.03E+08	0	1.03E+08	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0

[0678]

制程流名称→	烟道气	H ₂ O	H ₂ O	HCl 蒸气	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
MgCl ₂ *2W	0	0	0	0	0	4.08E+07	0
MgCl ₂ *4W	0	0	1.09E+07	0	0	0	0
MgCl ₂ *6W	0	0	1.83E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0.001	0	0	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
Mg ²⁺	0	0	0	0	3.74E+06	0	3.74E+06
Cl ⁻	0	0	0	0	1.09E+07	0	1.09E+07
CO ₃ ²⁻	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0
SiO ₂	0	0	0	0	0	0	9.24E+06
MgSiO ₃	0	0	0	0	0	0	174011.19

[0679]

表 18b. 关于实施例 14 和 15 模拟的质量和能量。

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
PH					.0864		6.24
温度 °C	26	25		200.7	60	250	95
压强 psia	14.696	14.696		15	44.088	14.696	44.088
质量蒸气分率	0	0		0	0	0	0
质量固体分率	1	1		1	0.248	1	0.268
质量流速 吨/年	1.31E+07	1.56E+07	0	9.41E+06	1.71E+08	2.39E+07	3.39E+07
体积流速 gal/min	1985.546	2126.004		1613.601	178707.499	3828.933	8016.874
焓 MW	0	-6925.208	0	0	-18961.843	-7057.974	-12123.17
密度 lb/cuft	187.864	208.902		165.967	27.184	177.393	120.206
H ₂ O	0	0		0	5.19E+06	0	1.00E+07
HCl	0	0		0	0	0	0
CO ₂	0	0		0	6.85E+06	0	0
O ₂	0	0		0	1.37E+07	0	0
N ₂	0	0		0	1.03E+08	0	0
MgCO ₃	1.31E+07	0		0	1.31E+07	0	0
MgCl ₂	0	0		0	0	0	0

[0680]

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
MgCl ₂ *W	0	0		0	0	0	0
MgCl ₂ *2W	0	0		0	0	0	0
MgCl ₂ *4W	0	0		0	1.09E+07	0	0
MgCl ₂ *6W	0	0		0	1.83E+07	0	0
Mg(OH)Cl	0	0		0	0	2.39E+07	0
Mg(OH) ₂	0	0		0	0	0	9.07E+06
MgO	0	0		0	0	0	0
MgHCO ₃ ⁺	0	0		0	0.001	0	0
SO ₂	0	0		0	0	0	0
NO ₂	0	0		0	0	0	0
NO	0	0		0	0	0	0
Mg ²⁺	0	0		0	0	0	3.78E+06
Cl ⁻	0	0		0	0	0	1.10E+07
CO ₃ ²⁻	0	0		0	0	0	0
HCO ₃ ⁻	0	0		0	0	0	0
OH ⁻	0	0		0	0	0	0.029
SiO ₂	0	0		9.24E+06	0	0	0

[0681]

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
MgSiO ₃	0	1.56E+07		174011.19	0	0	0

表 19a. 关于实施例 16 和 17 模拟的质量和能量。

制程流名称→	烟道气	H ₂ O	H ₂ O	HCl 蒸气	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
PH			6.583				
温度 °C	100	25	59.6	450	200	200	200
压强 psia	15.78	1	14.696	14.696	15	14.696	14.696
质量蒸气分率	1	0	0.004	1	0	0	0
质量固体分率	0	0	0	0	1	1	1
质量流速 吨/年	1.37E+08	1.00E+07	1.70E+07	1.41E+07	2.04E+07	2.04E+07	2.98e+07
体积流速 gal/min	6.21E+07	4569.619	40446.86	1.26E+07	1914.466	1914.466	3522.292
焓 MW	-5853.92	-4563.814	-7633.28	-1728.6	0	-5597.066	-9628.072
密度 lb/cuft	0.063	62.249	11.94	0.032	303.28	303.28	240.308
H ₂ O	685.E+06	1.00E+07	1.68E+07	2.80E+06	0	0	0
HCl	0	0	0	1.13E+07	0	0	0
CO ₂	1.37E+07	0	56280.04	0	0	0	0
O ₂	1.37E+07	0	18848.97	0	0	0	0

[0682]

制程流名称→	烟道气	H ₂ O	H ₂ O	HCl 蒸气	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
N ₂	1.03E+08	0	56346.51	0	0	0	0
MgCO ₃	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	2.04E+07	2.04E+07	2.04E+07
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	77.467	0	0	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
Mg ²⁺	0	0	744.857	0	0	0	0
Cl ⁻	0	0	0	0	0	0	0
CO ₃ ²⁻	0	0	1.19	0	0	0	0

[0683]

[0684]

制程流名称→	烟道气	H ₂ O	H ₂ O	HCl 蒸气	MgCl ₂ --2	MgCl ₂ -2w	MgCl ₂ -Si
HCO ₃ ⁻	0	0	3259.779	0	0	0	0
OH ⁻	0	0	0.109	0	0	0	0
SiO ₂	0	0	0	0	0	0	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0

表 19b. 关于实施例 16 和 17 模拟的质量和能量.

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
PH					6.583		8.537
温度 °C	59.6	25	60	200	60	450	95
压强 psia	14.696	14.696	44.088	15	44.088	14.696	44.088
质量蒸气分率	0	0	1	0	0	0	0
质量固体分率	1	1	0	1	0.436	1	0.558
质量流速 吨/年	1.31E+07	1.56E+07	1.23E+08	9.34E+06	3.01E+07	6.27E+06	1.63E+07
体积流速 gal/min	1983.661	2126.004	1.76E+07	1607.826	9945.342	797.11	5155.55
焓 MW	0	-6925.208	-1613.054	0	-12593.788	-2603.979	-7331.893
密度 lb/cuft	187.864	208.902	0.199	165.327	86.031	223.695	89.76
H ₂ O	0	0	0	0	1.68E+07	0	7.20E+06

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
HCl	0	0	0	0	0	0	0
CO ₂	0	0	6.78E+06	0	56280.036	0	0
O ₂	0	0	1.37E+07	0	18848.966	0	0
N ₂	0	0	1.03E+08	0	56346.51	0	0
MgCO ₃	1.31E+07	0	0	0	1.31E+07	0	0
MgCl ₂	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	9.07E+06
MgO	0	0	0	0	0	6.27E+06	0
MgHCO ₃ ⁺	0	0	343.415	0	77.467	0	0
SO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0

[0685]

[0686]

制程流名称→	MgCO ₃	MgSiO ₃	RX2-通气孔	SiO ₂	浆液	固体-1	固体-2
Mg ²⁺	0	0	2722.849	0	744.857	0	14.282
Cl ⁻	0	0	0	0	0	0	0
CO ₃ ²⁻	0	0	4.344	0	1.19	0	0
HCO ₃ ⁻	0	0	14439.982	0	3259.779	0	0
OH ⁻	0	0	0.481	0	0.109	0	19.989
SiO ₂	0	0	0	9.34E+06	0	0	0
MgSiO ₃	0	1.56E+07	0	0	0	0	0

表 20a. 关于实施例 18 和 19 模拟的质量和能量。

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通 气孔	HCl 蒸气 2	HCl 蒸气	HCl 通气 孔 2	熔化物 1	熔化物 2	熔化物 3
PH												
温度 °C	200	160	100	25	250	100	349.1	349.1	160	160	160	100
压强 psia	14.696	14.696	15.78	1	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
质量蒸气分率	0.378	0.473	1	0	1	1	1	1	1	0.311	0	0
质量固体分率	0.622	0	0	0	0	0	0	0	0	0.342	1	0.291
质量流速 吨/年	6.32E+07	2.40E+07	1.37E+08	1.00E+07	3.94E+07	0.001	197E+07	1.97E+07	26.688	3.65E+07	1.25E+07	3.22E+07

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通 气孔	HCl 蒸气 2	HCl 蒸气	HCl 通气 孔 2	熔化物 1	熔化物 2	熔化物 3
体积流速 gal/min	2.29E+07	1.02E+07	6.21E+07	4569.619	3.64E+07	0.001	1.82E+07	1.82E+07	11.834	1.02E+07	1866.916	9636.543
焓 MW	-19530.7	-8042.026	-5853.92	-4563.814	-11241.7	0	-5620.856	-5620.856	-0.002	-13498.19	-5456.154	-12759.563
密度 lb/cuft	0.079	0.067	0.063	62.249	0.031	0.075	0.031	0.031	0.064	0.102	190.163	94.933
H ₂ O	2.29E+07	1.54E+07	6.85E+06	1.00E+07	2.08E+07	0	1.40E+07	1.40E+07	0	1.54E+07	0	1.54E+07
HCl	983310.7	0	0	0	1.13E+07	0.001	5.67E+06	5.67E+06	26.688	26.688	0	0.001
CO ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
O ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
N ₂	0	0	1.03E+08	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	3.73E+07	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	2.07E+06	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0	0	0

[0687]

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通 气孔	HCl 蒸气 2	HCl 蒸气	HCl 通气 孔 2	熔化物 1	熔化物 2	熔化物 3
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	2494.617	0	0	0	0	0	0	0	2494.617	0	1.89E+06
Ca ²⁺	0	3.11E+06	0	0	0	0	0	0	0	3.11E+06	0	4128.267
Cl ⁻	0	5.51E+06	0	0	0	0	0	0	0	5.51E+06	0	5.51E+06
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	11965.659	11965.659	0
SiO ₂	0	0	0	0	0	0	0	0	0	4.67E+06	4.67E+06	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0	0	0	7.80E+06	7.80E+06	36.743
透辉石	0	0	0	0	0	0	0	0	0	0	0	0
白云石	0	0	0	0	0	0	0	0	0	0	0	0

[0688]

表 20b. 关于实施例 18 和 19 模拟的质量和能量。

制程流名称→	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
PH							5.163			6.252	
温度 °C	25	100	100	95	95	100	95	95	250	95	95
压强 psia	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
质量蒸气分率	0	0	0	0	0	0	0	0	0	0	1
质量固体分率	1	0	1	0.828	1	1	0.317	1	1	0.268	0
质量流速 吨/年	168E+07	2.28E+07	4.74E+07	5.73E+07	1.58E+07	9.34E+06	1.95E+08	1.43E+07	2.39E+07	3.39E+07	1.23E+08
体积流速 gal/min	1063.002	8028.716	8412.597	13075.55	2804.199	1607.827	185622	2276.765	3828.933	8017.333	5.85E+07
焓 MW	-7167.458	0	-16601.2	-21023.6	-5537.26	0	-27714.4	0	-7057.97	-12113.4	-1510.76
密度 lb/cuft	450.627	80.836	160.371	124.605	160.371	165.327	29.855	178.921	177.393	120.2	0.06
H ₂ O	0	1.54E+07	0	9.84E+07	0	0	9.84E+06	0	0	1.00E+07	0
HCl	0	0	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	6.85E+06	0	0	0	6.85E+06
O ₂	0	0	0	0	0	0	1.37E+07	0	0	0	1.37E+07
N ₂	0	0	0	0	0	0	1.03E+08	0	0	0	1.03E+08
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0

[0689]

制程流名称→	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	4.74E+07	4.74E+07	1.58E+07	0	4.74E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	2.39E+07	0	0
Mg(OH) ₂	0	0	0	12011.06	0	0	12011.06	0	0	9.07E+06	0
MgO	0	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	11.135	0	0	11.135	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	1.89E+06	0	0	0	0	0	0	0	3.78E+06	0
Ca ²⁺	0	4128.267	0	0	0	0	0	0	0	0	0
Cl ⁻	0	5.51E+06	0	4.627	0	0	4.627	0	0	1.10E+07	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0.03	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	0	0

[0690]

制程流名称→	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ --H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
SiO ₂	0	0	0	0	0	9.34E+06	0	0	0	0	0
MgSiO ₃	0	0	0	0	0	36.743	0	0	0	0	0
透辉石	1.68E+07	0	0	0	0	0	0	0	0	0	0
白云石	0	0	0	0	0	0	1.43E+07	1.43E+07	0	0	0

表 21a. 关于实施例 20 和 21 模拟的质量和能量。

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通气孔	HCl 蒸气 2	HCl 蒸气孔 2	熔化物 1	熔化物 2	熔化物 3
PH											
温度 °C	200	160	100	25	450	100	449.5	160	160	160	100
压强 psia	14.696	14.696	15.78	1	14.696	14.696	14.696	14.696	14.696	14.696	14.696
质量蒸气分率	0.378	0.256	1	0	1	1	1	1	0.148	0	0
质量固体分率	0.622	0	0	0	0	0	0	0	0.423	1	0.371
质量流速 吨/年	3.16E+07	1.70E+07	1.37E+08	1.00E+07	2.54E+07	0.006	1.27E+07	10.275	2.95E+07	1.25E+07	2.52E+07
体积流速 gal/min	1.14E+07	3.91E+06	6.21E+07	4569.619	2.94E+07	0.002	1.47E+07	4.556	3.91E+06	1866.915	6342.437
焓 MW	-9765.36	-5388.055	-5853.92	-4563.814	-5787.5	0	-2893.751	-0.0001	-10844.21	-5456.149	-9602.42
密度 lb/cuft	0.079	0.124	0.063	62.249	0.025	0.075	0.025	0.064	0.215	190.163	112.823

[0691]

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通气 孔	HCl 蒸气 2	HCl 蒸气	HCl 通气 孔 2	熔化物 1	熔化物 2	熔化物 3
H ₂ O	1.15E+07	8.41E+06	6.85E+06	1.00E+07	1.40E+07	0	7.00E+06	7.00E+06	0	8.41E+06	0	8.41E+06
HCl	491655.4	0	0	0	1.13E+07	0.006	5.67E+06	5.67E+06	10.275	10.275	0	0.006
CO ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
O ₂	0	0	1.37E+07	0	0	0	0	0	0	0	0	0
N ₂	0	0	1.03E+08	0	0	0	0	0	0	0	0	0
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	1.86E+07	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *6W	0	0	0	0	0	0	0	0	0	0	0	0
Mg(OH)Cl	1.04E+06	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	0	0	0	0	0	0	0	0	0
MgO	0	0	0	0	0	0	0	0	0	0	0	0
MgHCO ₃ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0	0

[0692]

制程流名称→	5	CaCl ₂ -2W	烟道气	H ₂ O	HCl	HCl-通气孔	HCl 蒸气 2	HCl 蒸气	HCl 通气孔 2	熔化物 1	熔化物 2	熔化物 3
NO	0	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	2494.624	0	0	0	0	0	0	0	2494.624	0	1.89E+06
Ca ²⁺	0	3.11E+06	0	0	0	0	0	0	0	3.11E+06	0	4119.258
Cl ⁻	0	5.51E+06	0	0	0	0	0	0	0	5.51E+06	0	5.51E+06
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0	0	0	0	0	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	11939.54711939.547	0	0
SiO ₂	0	0	0	0	0	0	0	0	0	4.67E+06	4.67E+06	9.34E+06
MgSiO ₃	0	0	0	0	0	0	0	0	0	7.80E+06	7.80E+06	14.153
透辉石	0	0	0	0	0	0	0	0	0	0	0	0
白云石	0	0	0	0	0	0	0	0	0	0	0	0

表 21b. 关于实施例 20 和 21 模拟的质量和能量.

制程流名称→	MgCaSiO3	MgCl ₂ --H	MgCl ₂ -H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
PH				-0.879			5.271			8.545	

[0693]

制程流名称→	MgCaSiO3	MgCl ₂ --H	MgCl ₂ -H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
温度 °C	25	100	100	95	95	100	95	95	450	95	95
压强 psia	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696	14.696
质量蒸气分率	0	0	0	0	0	0	0	0	0	0	1
质量固体分率	1	0	1	0	0.484	1	1	0.177	1	1	0.558
质量流速 吨/年	1.68E+07	1.58E+07	1.58E+07	3.27E+07	1.58E+07	9.34E+06	1.70E+08	1.43E+07	6.27E+06	1.63E+07	1.23E+08
体积流速 gal/min	1063.002	4734.61	2804.199	10786.59	2804.199	1607.826	183332.5	2276.772	797.11	5155.892	5.85E+07
焓 MW	-7167.458	0	-5533.74	-13087	-5537.26	0	-19788.2	0	-2603.98	-7331.92	-1510.64
密度 lb/cuft	450.627	94.994	160.371	86.167	160.371	165.327	26.409	178.921	223.695	89.754	0.06
H ₂ O	0	8.41E+06	0	1.68E+07	0	0	1.68E+07	0	0	7.20E+06	0
HCl	0	0	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	6.85E+06	0	0	0	6.85E+06
O ₂	0	0	0	0	0	0	1.37E+07	0	0	0	1.37E+07
N ₂	0	0	0	0	0	0	1.03E+08	0	0	0	1.03E+08
MgCl ₂	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *2W	0	0	0	0	0	0	0	0	0	0	0
MgCl ₂ *4W	0	0	0	0	0	0	0	0	0	0	0

[0694]

制程流名称→	MgCaSiO ₃	MgCl ₂ --H	MgCl ₂ -H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
MgCl ₂ *6W	0	0	1.58E+07	1.58E+07	1.58E+07	0	1.58E+07	0	0	0	0
Mg(OH)Cl	0	0	0	0	0	0	0	0	0	0	0
Mg(OH) ₂	0	0	0	11678.01	0	0	11678.01	0	0	9.07E+06	0
MgO	0	0	0	0	0	0	0	0	6.27E+06	0	0
MgHCO ₃ ⁺	0	0	0	908.901	0	0	908.901	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0
Mg ²⁺	0	1.89E+06	0	0	0	0	0	0	0	14.555	0
Ca ²⁺	0	4119.258	0	0	0	0	0	0	0	0	0
Cl ⁻	0	5.51E+06	0	377.667	0	0	377.667	0	0	0	0
CO ₃ ²⁻	0	0	0	0	0	0	0	0	0	0	0
HCO ₃ ⁻	0	0	0	0.006	0	0	0.006	0	0	0	0
OH ⁻	0	0	0	0	0	0	0	0	0	0	0
CaSiO ₃	0	0	0	0	0	0	0	0	0	0	0
SiO ₂	0	0	0	0	0	9.34E+06	0	0	0	0	0
MgSiO ₃	0	0	0	0	0	14.153	0	0	0	0	0

[0695]

制程流名称→	MgCaSiO3	MgCl2--H	MgCl2-H	再循环	再循环-	SiO ₂	浆液	固体	固体-1	固体-2	通气孔
透辉石	1.68E+07	0	0	0	0	0	0	0	0	0	0
白云石	0	0	0	0	0	0	1.43E+07	1.43E+07			

- [0696] 实施例 22：其他盐的分解。
- [0697] 在实验室中测量其他盐的热分解。一些测试结果的汇总示于下表中。

[0698] 表 22. 其他盐的分解。

[0699]

盐	温度 °C	时间 (min.)	结果
Mg(NO ₃) ₂	400	30	分解 63%。反应为 $\text{Mg(NO}_3)_2 \rightarrow \text{MgO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$
Mg(NO ₃) ₂	400	45	分解 64% .
Mg(NO ₃) ₂	400	90	分解 100%
Mg(NO ₃) ₂	400	135	分解 100%
Ca(NO ₃) ₂	400	30	分解<25%，反应为 $\text{Ca(NO}_3)_2 \rightarrow \text{CaO} + 2\text{NO}_2 + \frac{1}{2} \text{O}_2$
Ca(NO ₃) ₂	600	50	分解 61%
Ca(NO ₃) ₂	600	过夜	分解 100%
LiCl	450	120	分解~0%

[0700] 实施例 22 :2 室、3 室和 4 室分解模型

[0701] 表 23(参见下文) 是对应于图 31-34 的 4 种设置的比较。描述的是室的数量和说明、所消耗的热 (以 MW(兆瓦) 表示)、来自特定源的热百分比和所需外部热的减小 (以 kW-H/ 吨 CO₂ 表示, 该减小是由于可得自制程中的其他反应 (即盐酸与硅酸盐矿物质的反应和盐酸的冷凝) 的热)。在图 34 的实施例中, 来自开放式循环天然气厂的热烟道气也适合。

[0702] 实施例 23 :输出矿物质与输入矿物质——煤的比较

[0703] 在涉及来自基于煤的发电厂的烟道气的此情形研究中, 表 24 阐明, 输出矿物质 (石灰石和沙) 的体积是输入矿物质 (煤和链状硅酸盐) 的体积的 83%。表 24 中所汇总的结果是基于 600MWe 煤工厂 ; 总共 4. 66E6 吨 CO₂, 包括用于制程所需热的 CO₂。

[0704] 实施例 24 :输出矿物质与输入矿物质——天然气的比较

[0705] 在表 25(下文) 中所汇总的涉及来自基于天然气的发电厂的烟道气的此情形研究中, 矿物质的“驶出体积 (rail-back volume)”是矿物质的“驶入体积 (rail-in volume)”的 92%。表 25 中所汇总的结果是基于 600MWe CC 天然气厂 ; 总共 2. 41E6 吨 CO₂, 其包括用于制程所需热的 CO₂。

[0706] 表 23. 2 室、3 室和 4 室分解结果

[0707]

		室描述				
实施例	室数量	预加热冷 烟道气	来自蒸汽 的预加热	预加热矿物质溶解反 应器		分解
				硅酸盐反 应	HCl 热回 收	
图 31 冷烟道气预加热	3					
热, MW		83.9	未使用	286	563	86.8
总热的百分比		8.2%	未使用	28.0%	55.2%	8.5%
减少, kW-Hr/吨		-506.7	未使用	-1727.4	-3400.5	未减少
图 32 冷烟道气和蒸汽 预加热	4					
热, MW		83.9	8.7	286	563	82.2
总热的百分比		8.2%	0.8%	27.9%	55.0%	8.0%
减少, kW-Hr/吨		-506.7	-52.5	-1727.4	-3400.5	未减少
图 33 仅天然气	2					
热, MW		未使用	未使用	279	586	129.3
总热的百分比		未使用	未使用	28%	59%	13%
减少, kW-Hr/吨		未使用	未使用	-1685.1	-3539.4	未减少
图 34 仅热烟道气	2					
热, MW		未使用	未使用	243	512	112.9
总热的百分比		未使用	未使用	28%	59%	13%
减少, kW-Hr/吨		未使用	未使用	-1467.7	-3092.4	-681.9

[0708] 表 24. 煤情形——输出矿物质体积与输入矿物质体积的比较
[0709]

		公制单位		英制单位	
参数	体积密度 (吨/m ³)	质量 (10 ⁶ 吨/年)	体积 (10 ⁶ m ³ /年)	质量 (10 ⁶ 吨/年)	体积 (10 ⁶ ft ³ /年)
煤	0.8	1.57	1.97	1.73	69.5
CaSiO ₃	0.71	12.30	17.32	13.56	611.8
煤 + CaSiO ₃					681.25
CaCO ₃	0.9	10.60	11.78	11.68	415.9
SiO ₂	1.5	6.35	4.23	7.00	149.5
CaCO ₃ + SiO ₂	n/a	16.95	16.01	18.68	565.4
输出矿物质体积/输入矿物质体积之比=					83.00%

[0710] 表 25. 天然气情形——输出矿物质体积与输入矿物质体积的比较

[0711]

		公制单位		英制单位	
参数	体积密度 (吨/m ³)	质量 (10 ⁶ 吨/年)	体积 (10 ⁶ m ³ /年)	质量 (10 ⁶ 吨/年)	体积 (10 ⁶ ft ³ /年)
煤	0.8	1.57	1.97	1.73	69.5
CaSiO ₃	0.71	12.30	17.32	13.56	611.8
煤 + CaSiO ₃					681.25
CaCO ₃	0.9	10.60	11.78	11.68	415.9
SiO ₂	1.5	6.35	4.23	7.00	149.5
CaCO ₃ + SiO ₂	n/a	16.95	16.01	18.68	565.4
输出矿物质体积/输入矿物质体积之比=					83.00%

[0712] 实施例 25 :通过水和氯化镁的歧化来选择性产生氢氧化镁

[0713] $\text{Mg}(\text{OH})_2$ 可用于下列反应以自 CO_2 气体产生石灰石。

[0714] $\text{CaCl}_2(\text{aq}) + \text{CO}_2 + \text{Mg}(\text{OH})_2 = \text{MgCl}_2(\text{aq}) + \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$

[0715] 为优化 $\text{Mg}(\text{OH})_2$ 的产生,在将 MgCl_2 转化成 $\text{Mg}(\text{OH})\text{Cl}$ 后,调节反应室中的水量以促进 $\text{Mg}(\text{OH})_2$ 沉淀。具体而言,在将 $\text{Mg}(\text{OH})\text{Cl}$ 和 MgCl_2 提供于足够大体积的水中时,氢氧化镁因实际上不溶而发生沉淀,而氯化镁形成水溶液。因此可以有效分离两种化合物。注意:以下反应中的水 (H_2O) 并不变为产物的一部分,其仅使 Mg^{2+} 和 Cl^- 溶剂化,从而使它们变为离子溶液。

[0716] $\text{Mg}(\text{OH})\text{Cl}(\text{H}_2\text{O}) = \text{Mg}(\text{OH})_2 \downarrow + \text{MgCl}_2(\text{aq})$

[0717] 若减小水量直至相对于镁的比率约为 6:1 为止,则可能形成 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 而非 $\text{MgCl}_2(\text{aq})$ 。其式如下:

[0718] $\text{Mg}(\text{OH})\text{Cl} + 3\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 \downarrow + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

[0719] 因此,通过维持 MgCl_2 与水的比率大于或等于 6:1,则倾向于产生 MgCl_2 水溶液和固体 $\text{Mg}(\text{OH})_2$ 。因此, CO_2 捕获反应的实例组可表示为:

[0720] i) $\text{MgCl}_2 \cdot \text{H}_2\text{O} = \text{Mg}(\text{OH})\text{Cl} + \text{H}_2\text{O} + \text{HCl}$

[0721] ii) $\text{HCl} + \text{CaSiO}_3 = \text{CaCl}_2 + \text{H}_2\text{O} + \text{SiO}_2$

[0722] iii) $\text{Mg}(\text{OH})\text{Cl} + \text{MgCl}_2 + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{MgCl}_2 + \text{H}_2\text{O}$

[0723] iv) $\text{H}_2\text{O} + \text{Mg}(\text{OH})_2 + \text{CO}_2 + \text{CaCl}_2 = \text{MgCl}_2 + \text{CaCO}_3 + \text{H}_2\text{O}$

[0724] 总反应为: $\text{CaSiO}_3\text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2$ 。

[0725] 此系统示于图 38A-I 和图 39A-I 的 Aspen 图中。在图中部所描绘的矩形围绕所定义“水歧化器”。在矩形的顶部, $\text{Mg}(\text{OH})\text{Cl}$ (流固体 -1) 离开标记为“分解 (DECOMP)”的分解反应器。然后,在标记为 MGOH2 的模块中,使 $\text{Mg}(\text{OH})\text{Cl}$ 与来自吸收塔的 MgCl_2 水溶液 (流 - 再循环 2) 混合。其以浆液形式 (流“4”) 自单元离开,通过热交换器且将热输送至分解室。该流然后称为“13”,其通过分离单元,该分离单元将流分离成流 MGCLSLRY (大部分为 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) 和流固体 -2 (其是流向吸收塔的 $\text{Mg}(\text{OH})_2$)。

[0726] 根据本公开内容无需过多实验即可获得并实施本文所公开和主张的所有方法。尽管已根据具体实施方案描述本发明的组合物和方法,但本领域技术人员将了解,可改变这些方法和本文所述方法的步骤或步骤的顺序,这并不背离本发明的概念、精神和范围。对本领域技术人员显而易见的所有这些类似替代物和修改均视为在由所附权利要求书所定义的本发明的精神、范围和概念内。

[0727] 参考文献

[0728] 下列参考文献以引用方式并入本文中至其提供示例性程序或者补充本文所述的细节的程度。

[0729] 美国临时申请第 60/612,355 号

[0730] 美国临时申请第 60/642,698 号

[0731] 美国临时申请第 60/718,906 号

[0732] 美国临时申请第 60/973,948 号

[0733] 美国临时申请第 61/032,802 号

[0734] 美国临时申请第 61/033,298 号

- [0735] 美国临时申请第 61/288,242 号
- [0736] 美国临时申请第 61/362,607 号
- [0737] 美国专利申请第 11/233,509 号
- [0738] 美国专利申请第 12/235,482 号
- [0739] 美国专利公开第 2006/0185985 号
- [0740] 美国专利公开第 2009/0127127 号
- [0741] 美国专利第 7,727,374 号
- [0742] PCT 申请第 PCT/US08/77122 号
- [0743] Goldberg et al., Proceedings of First National Conference on Carbon Sequestration, 14 - 17 May 2001, Washington, DC., section 6c, United States Department of Energy, National Energy Technology Laboratory. 可得自: http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/6c1.pdf
- [0744] Proceedings of First National Conference on Carbon Sequestration, 14 - 17 May 2001, Washington, DC. United States Department of Energy, National Energy Technology Laboratory. CD-ROM USDOE/NETL-2001/1144; 也可得自 http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/carbon_seq01.html
- [0745] de Bakker, The Recovery of Magnesium Oxide and Hydrogen Chloride from Magnesium Chloride Brines and Molten Salt Hydrates, March 2011, Queens University, Kingston, Ontario, Canada. Thesis by Jan Simon Christiaan de Bakker; 也可得自互联网 [qspace.library.queensu.ca/bitstream/1974/6337/1/de % 20Bakker_Jan_SC_201103_PhD.pdf](http://qspace.library.queensu.ca/bitstream/1974/6337/1/de%20Bakker_Jan_SC_201103_PhD.pdf)

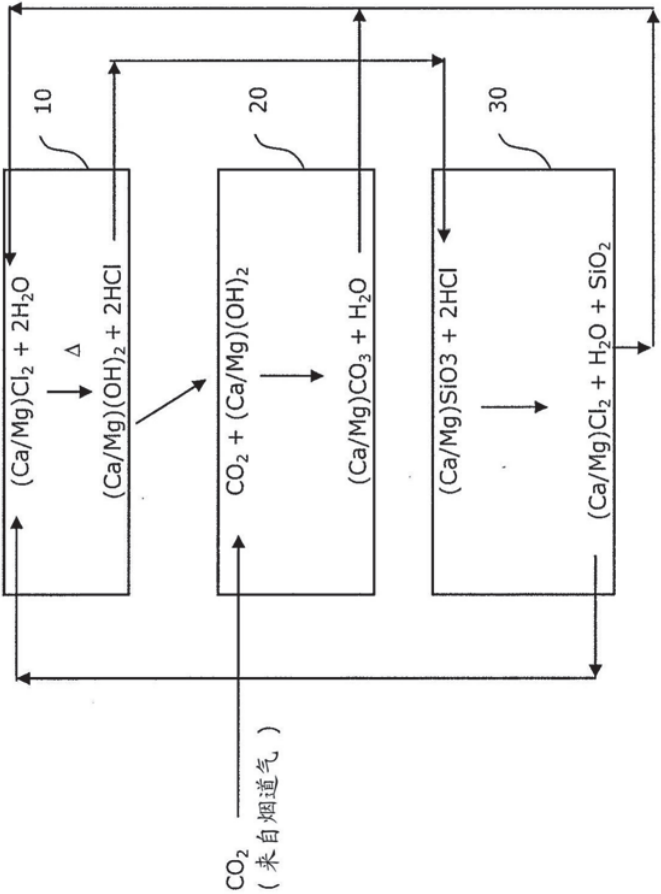


图 1

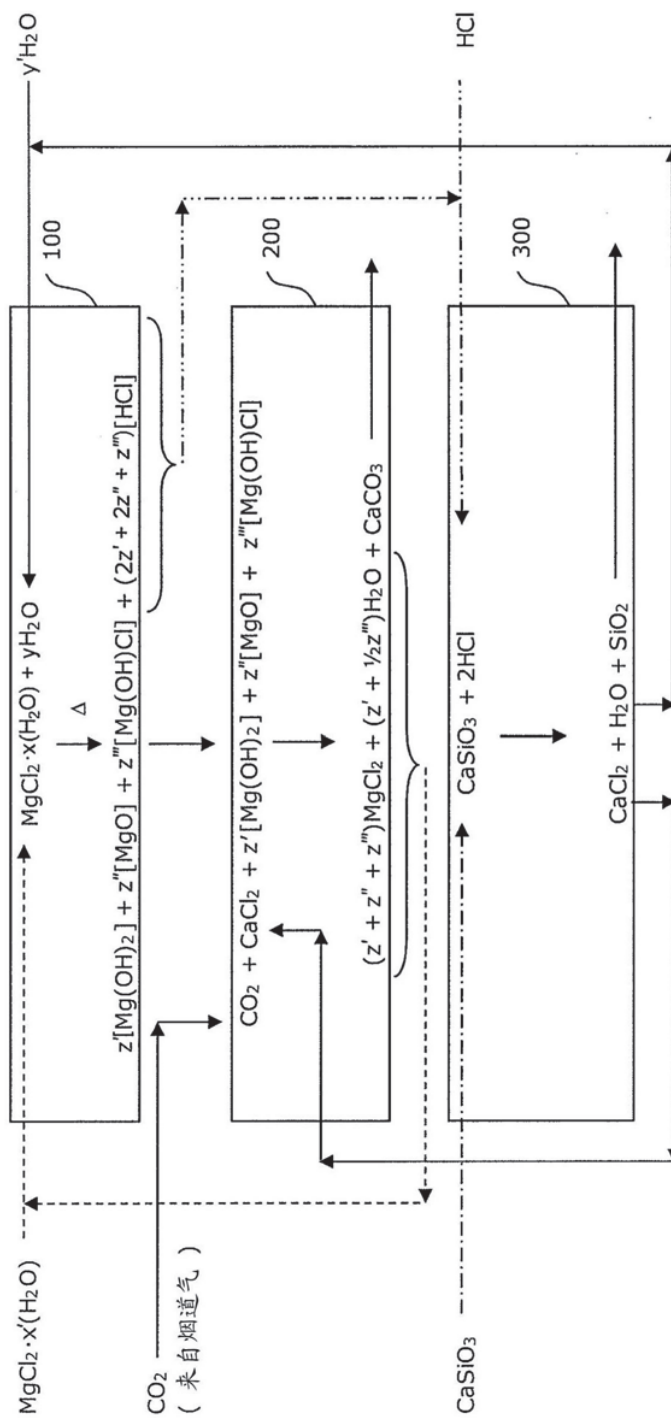


图 2

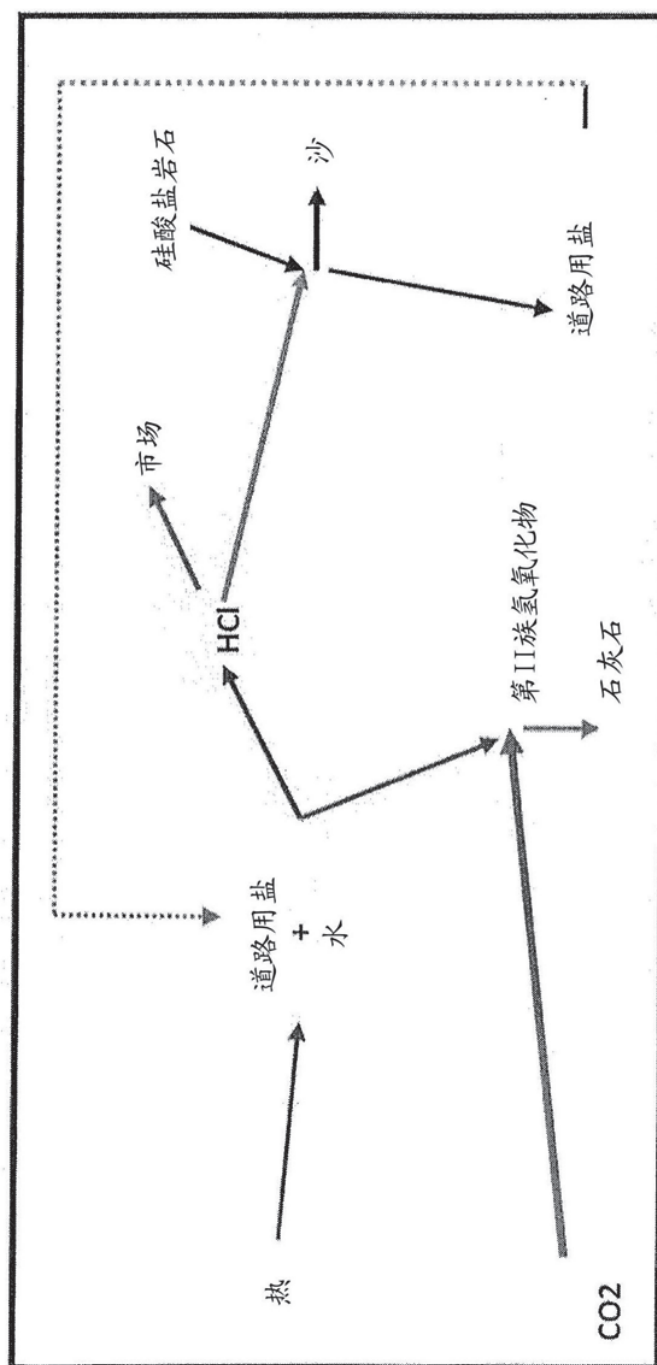


图 3

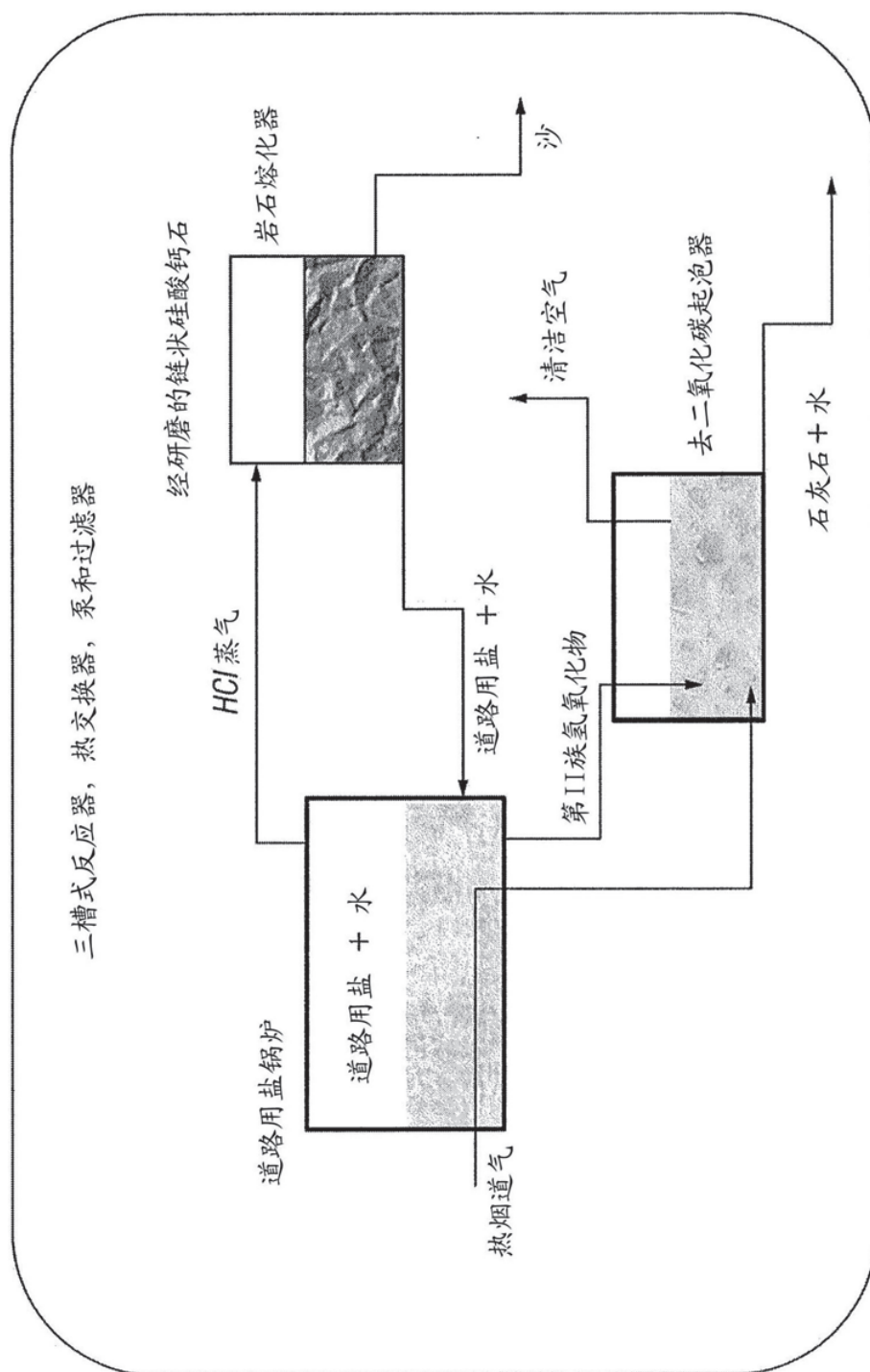


图 4

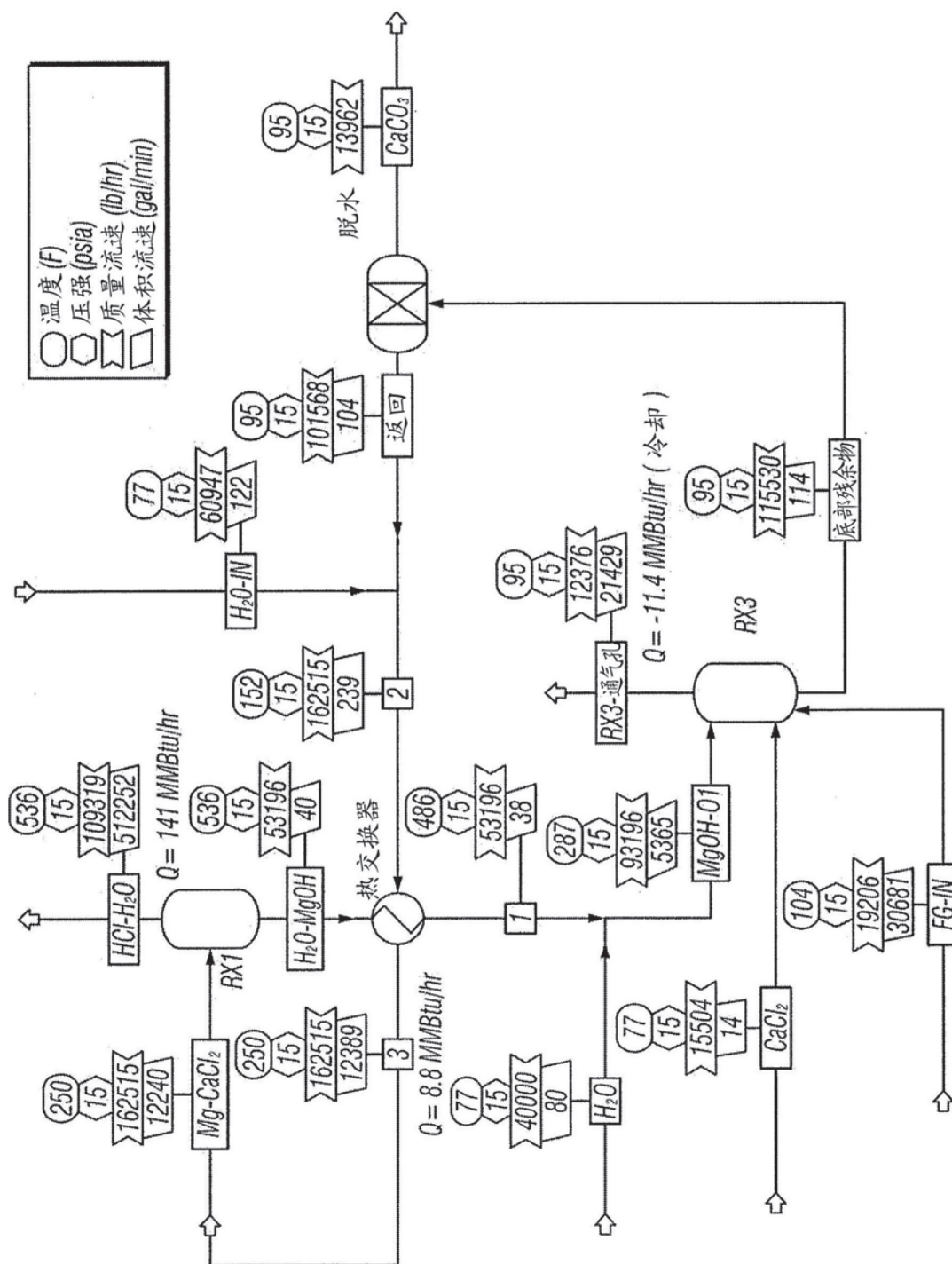


图 5

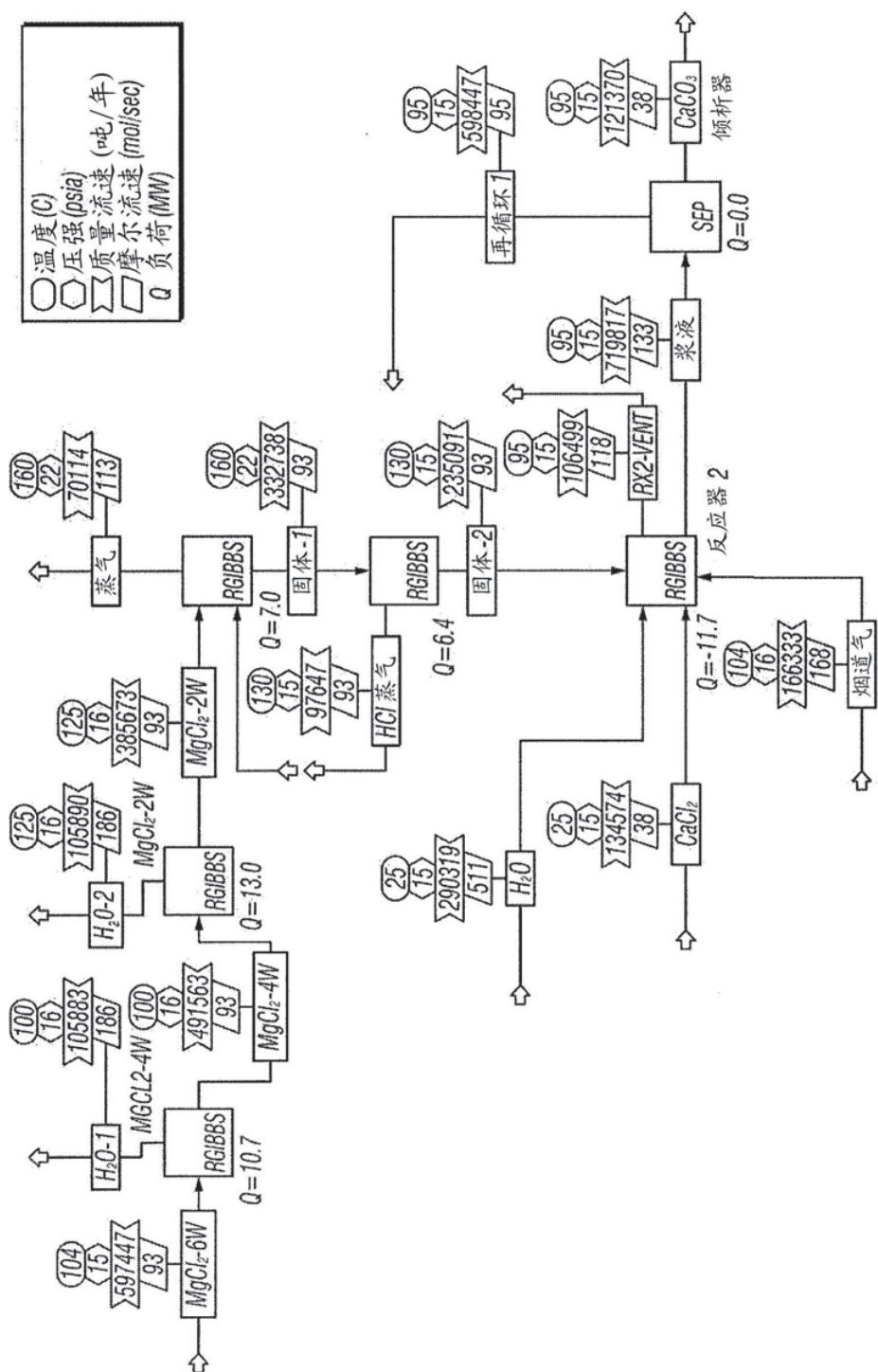


图 6

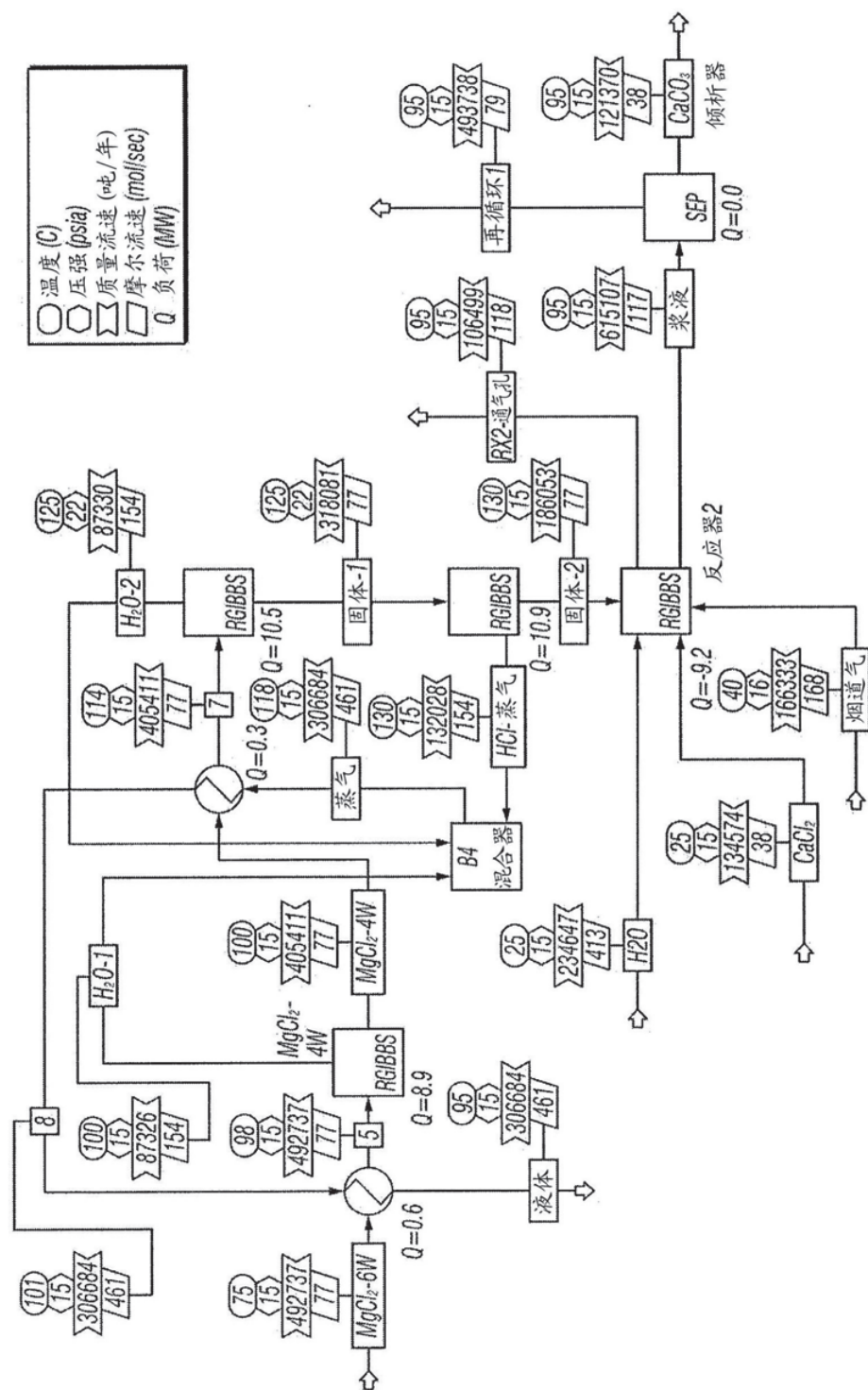


图 7

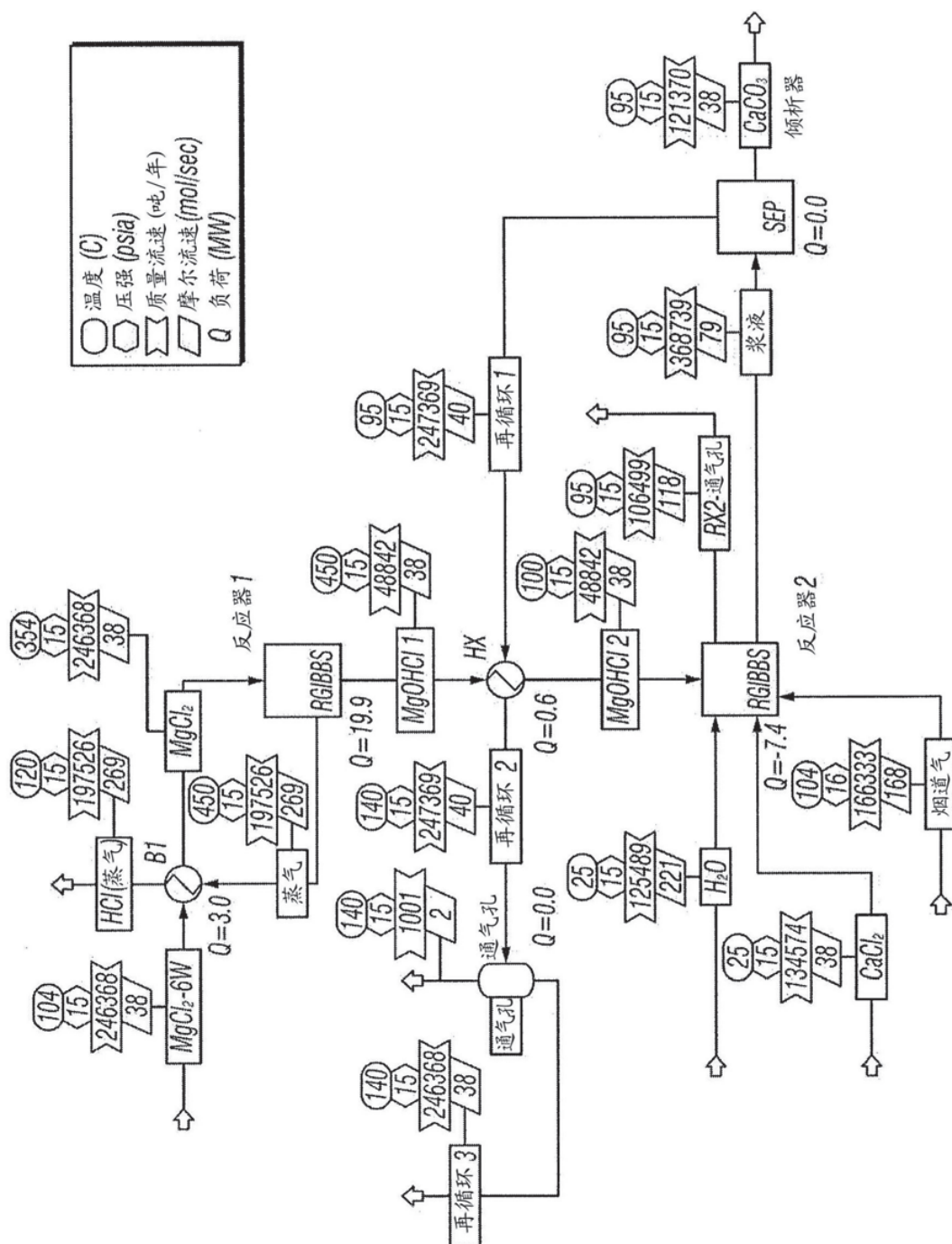


图 8

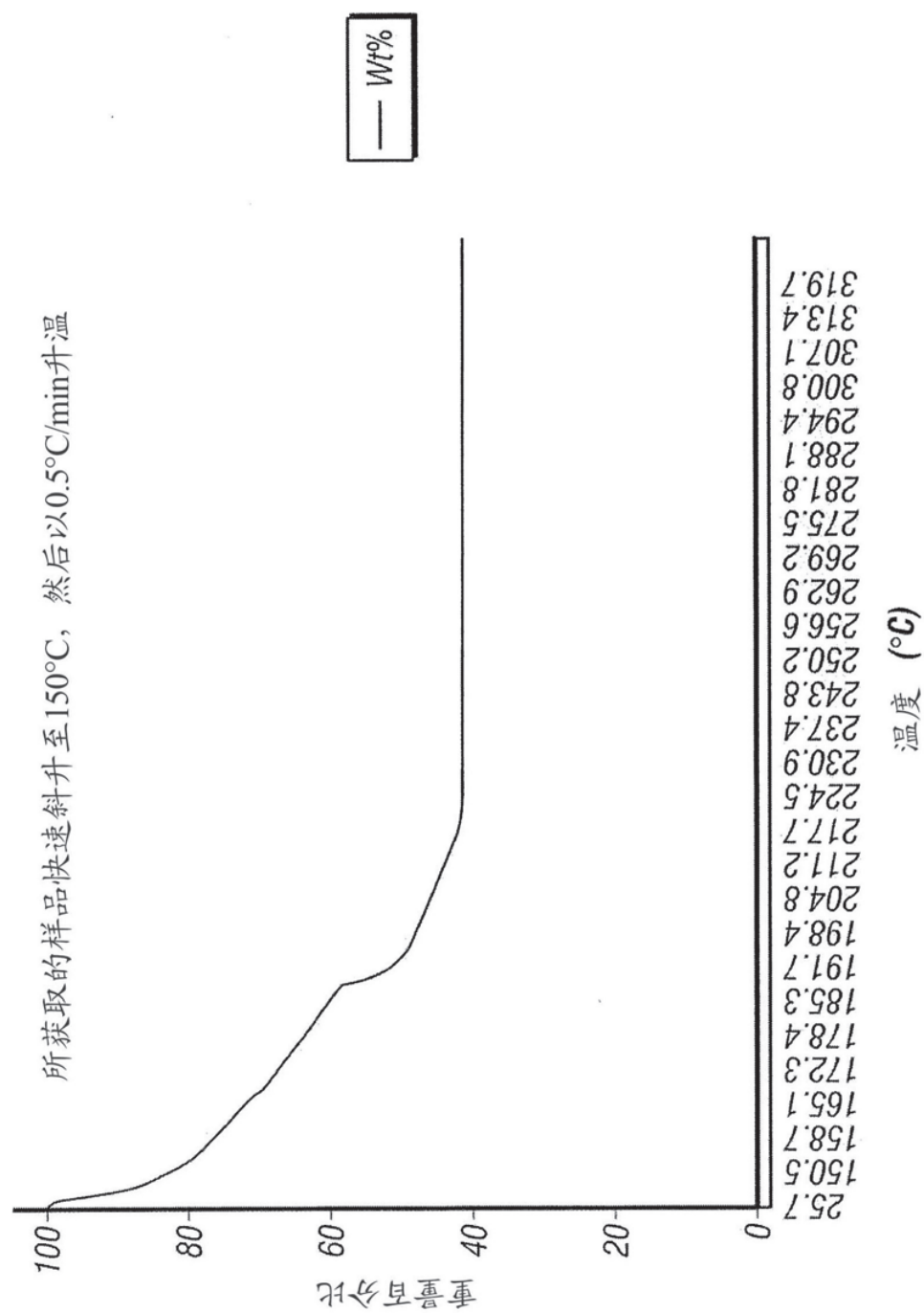


图 10

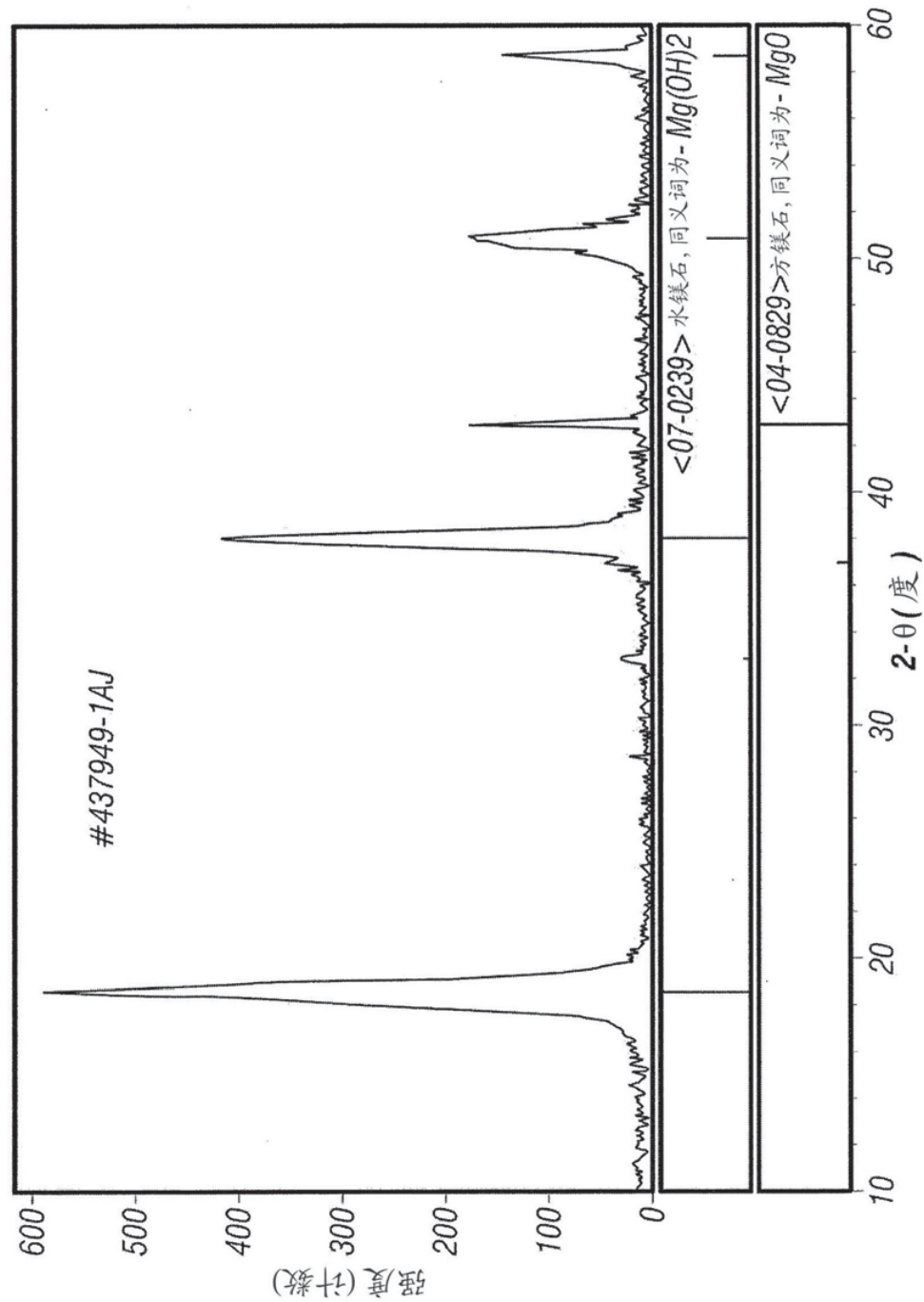


图 11

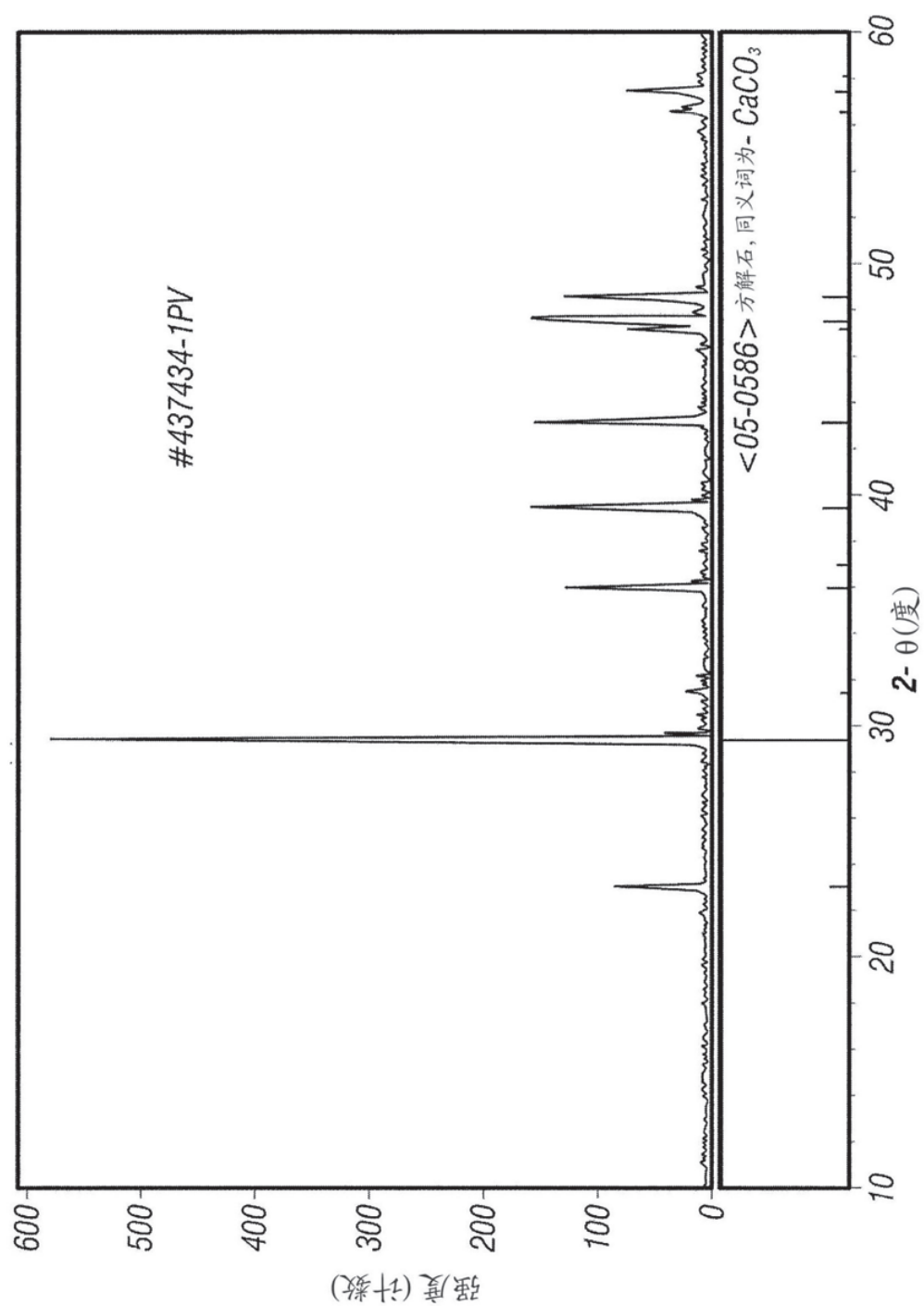


图 12

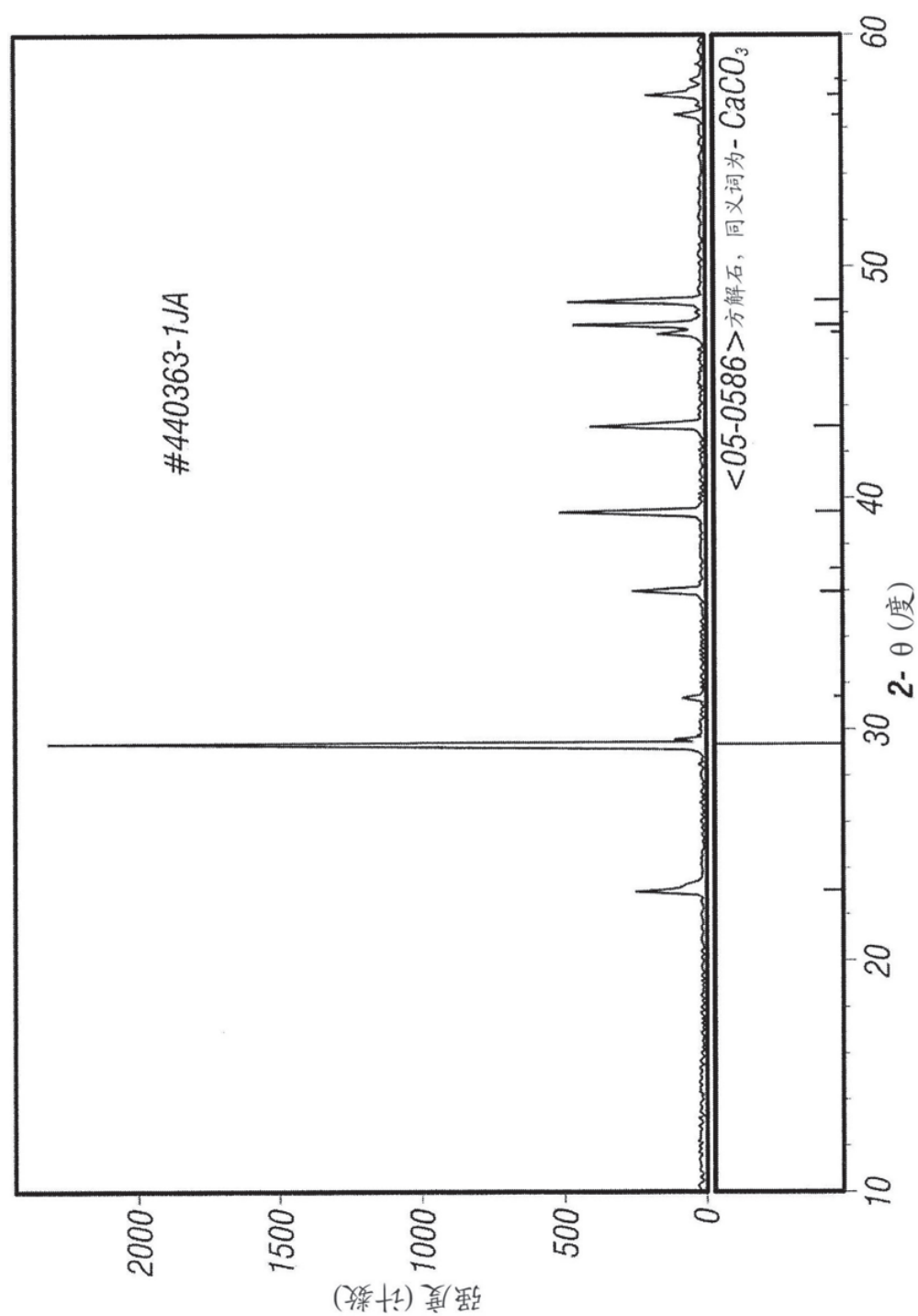


图 13

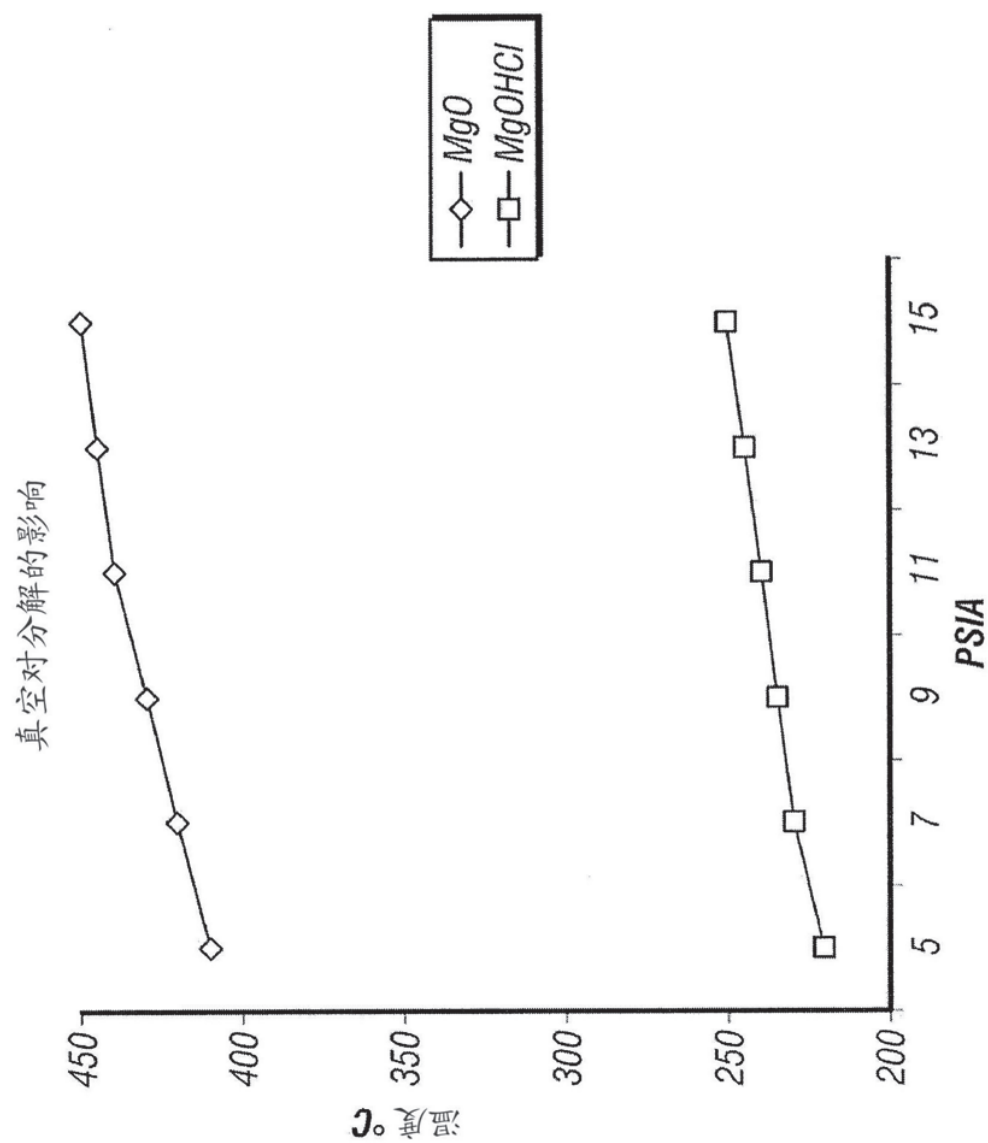


图 14

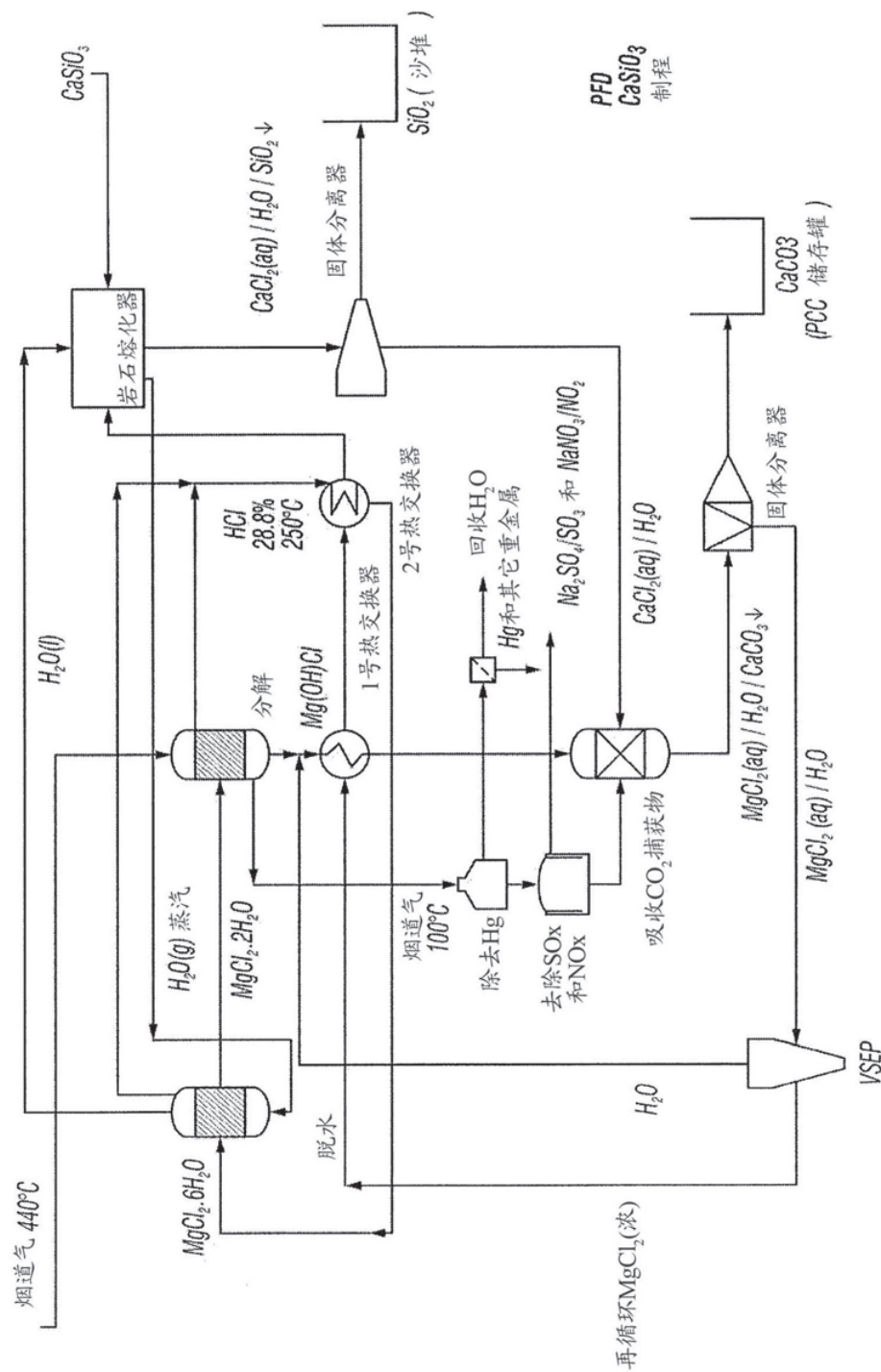


图 15

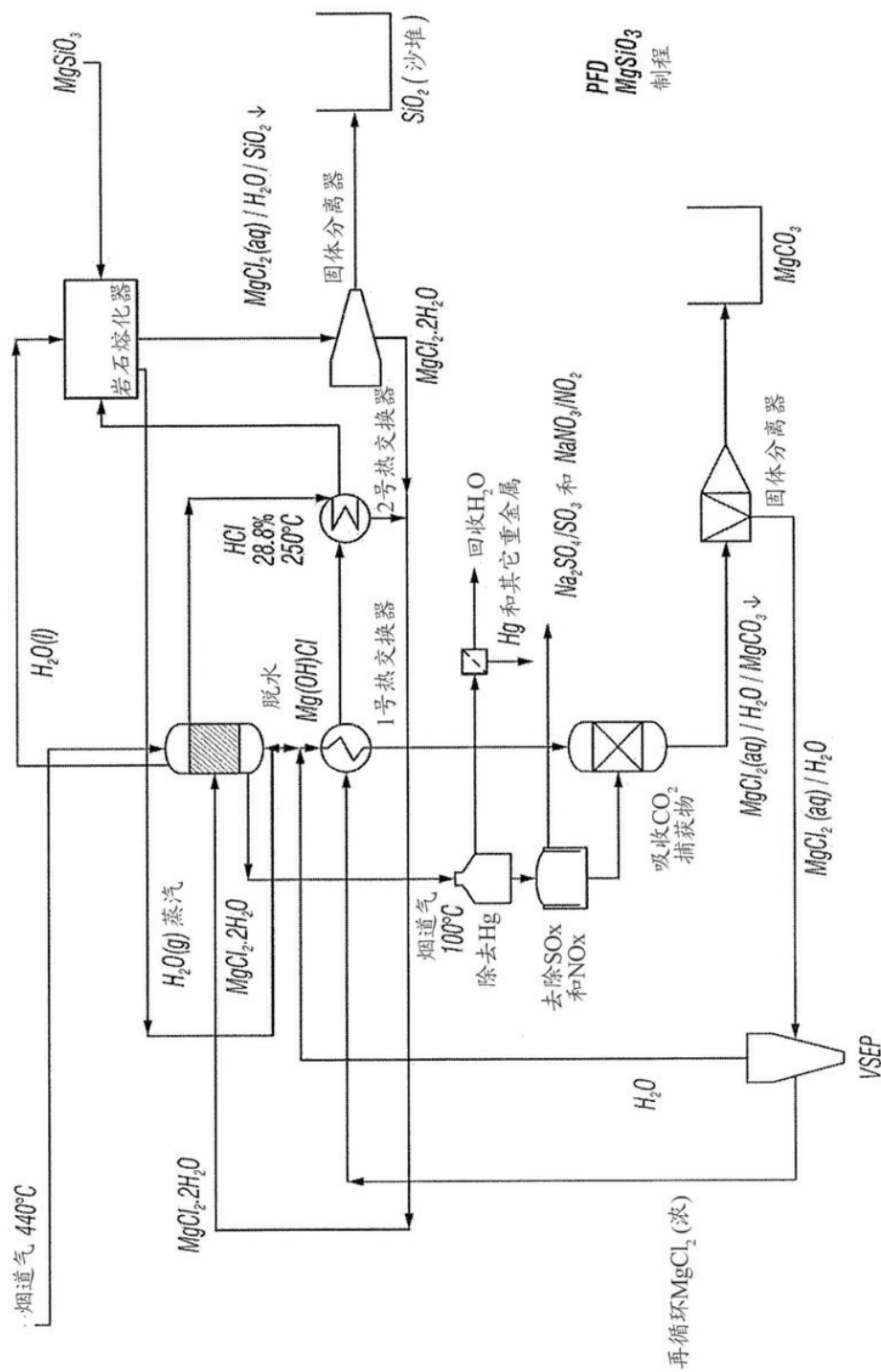


图 16

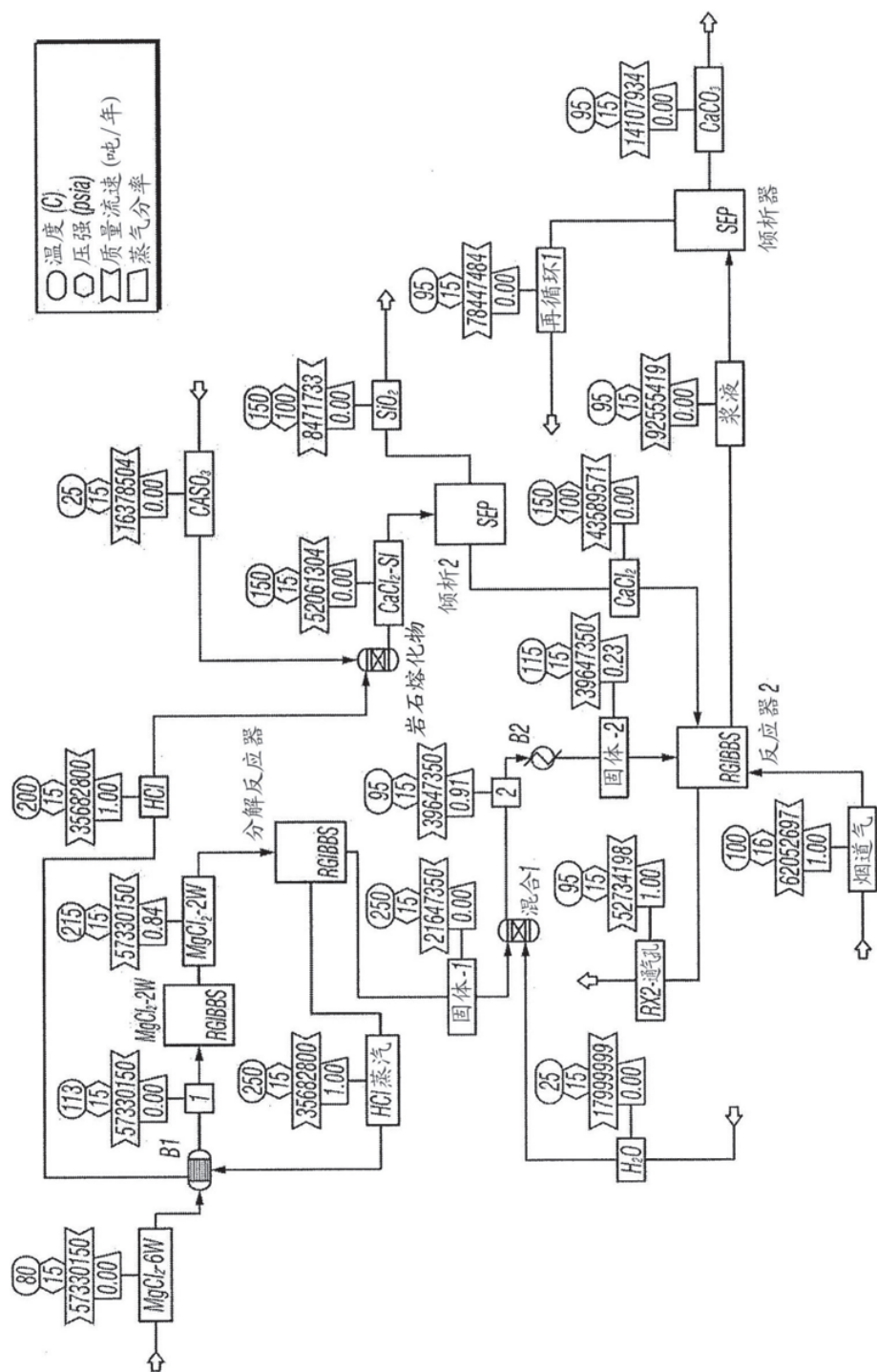


图 18

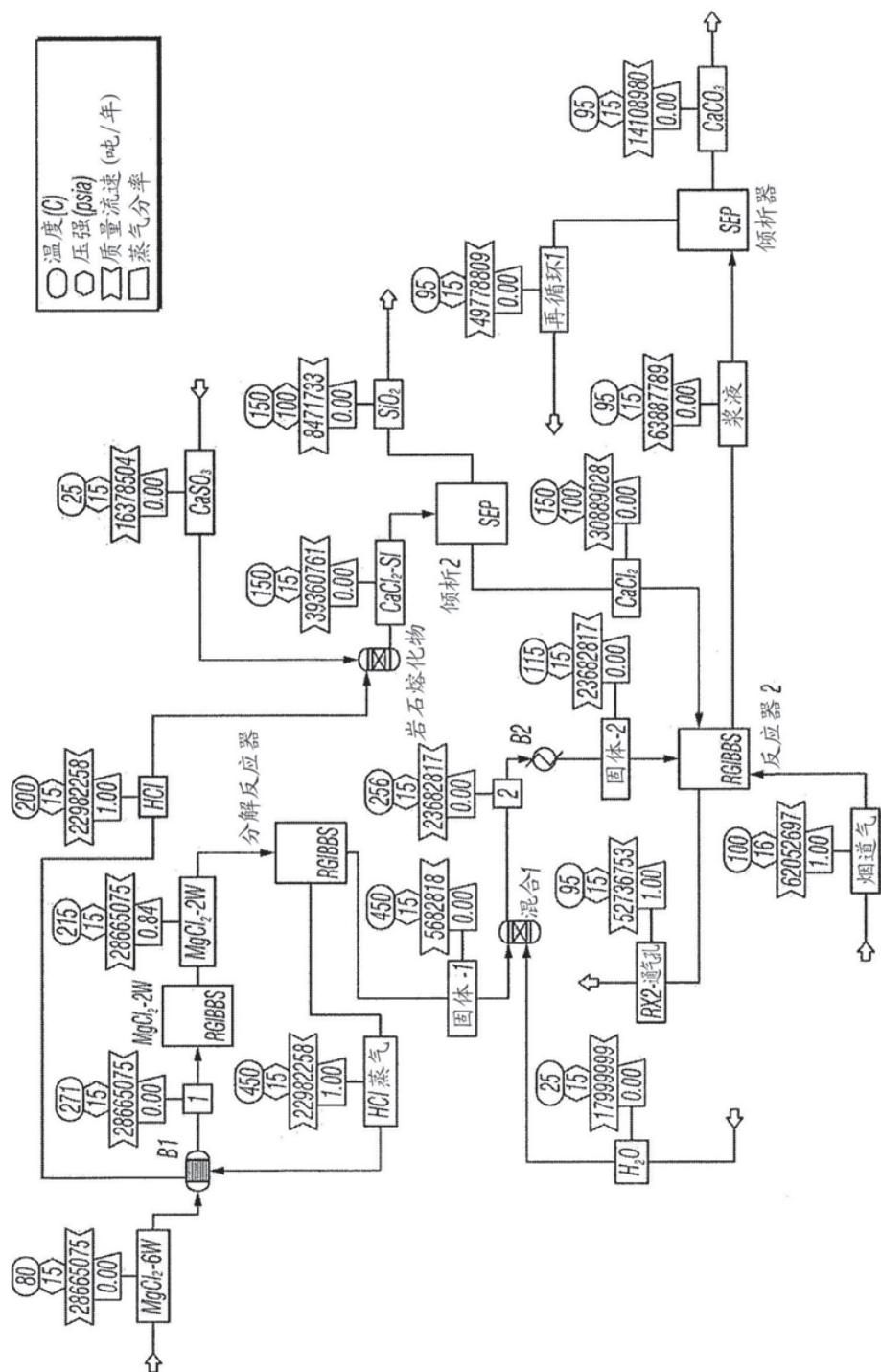


图 19

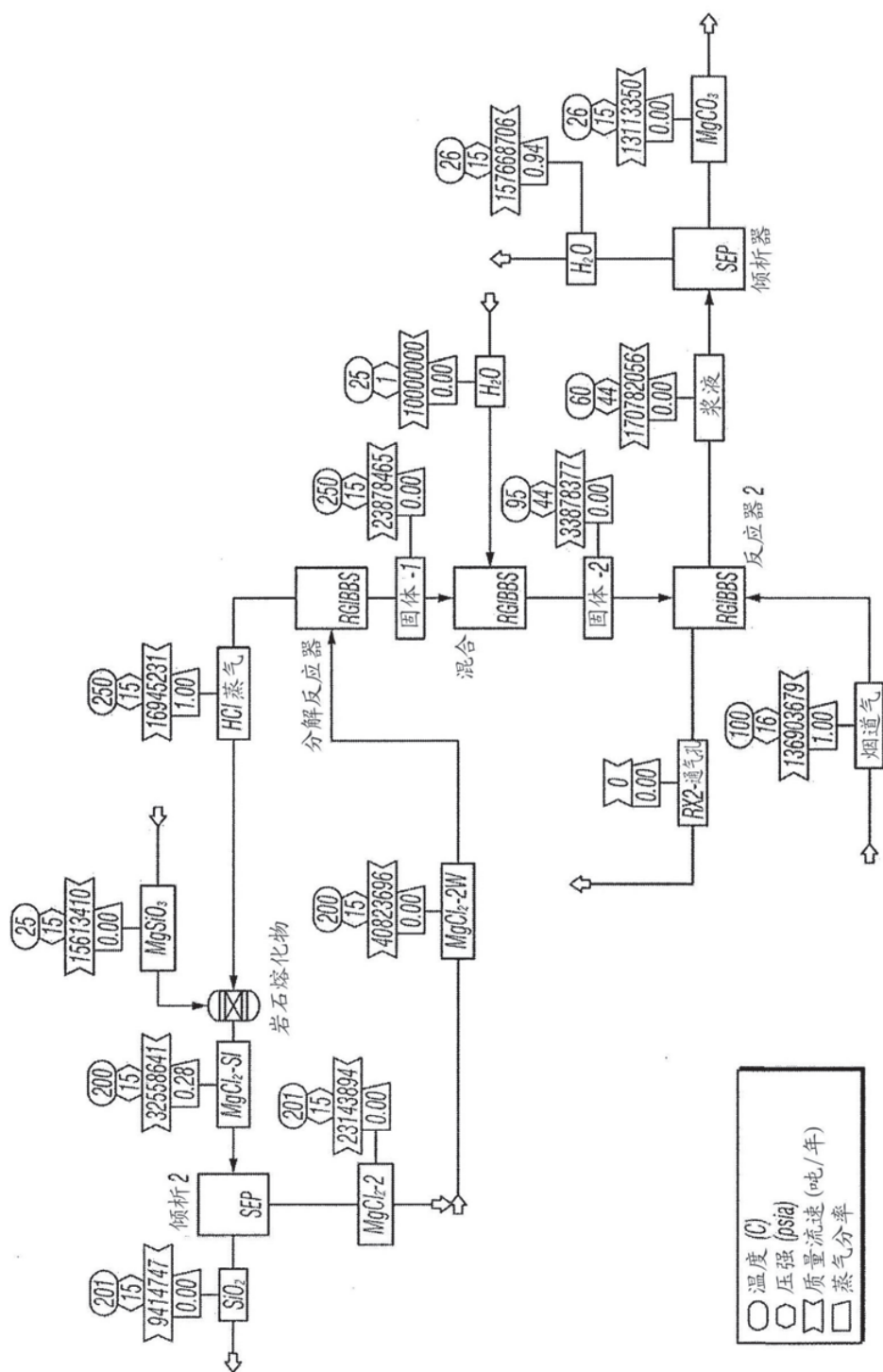


图 20

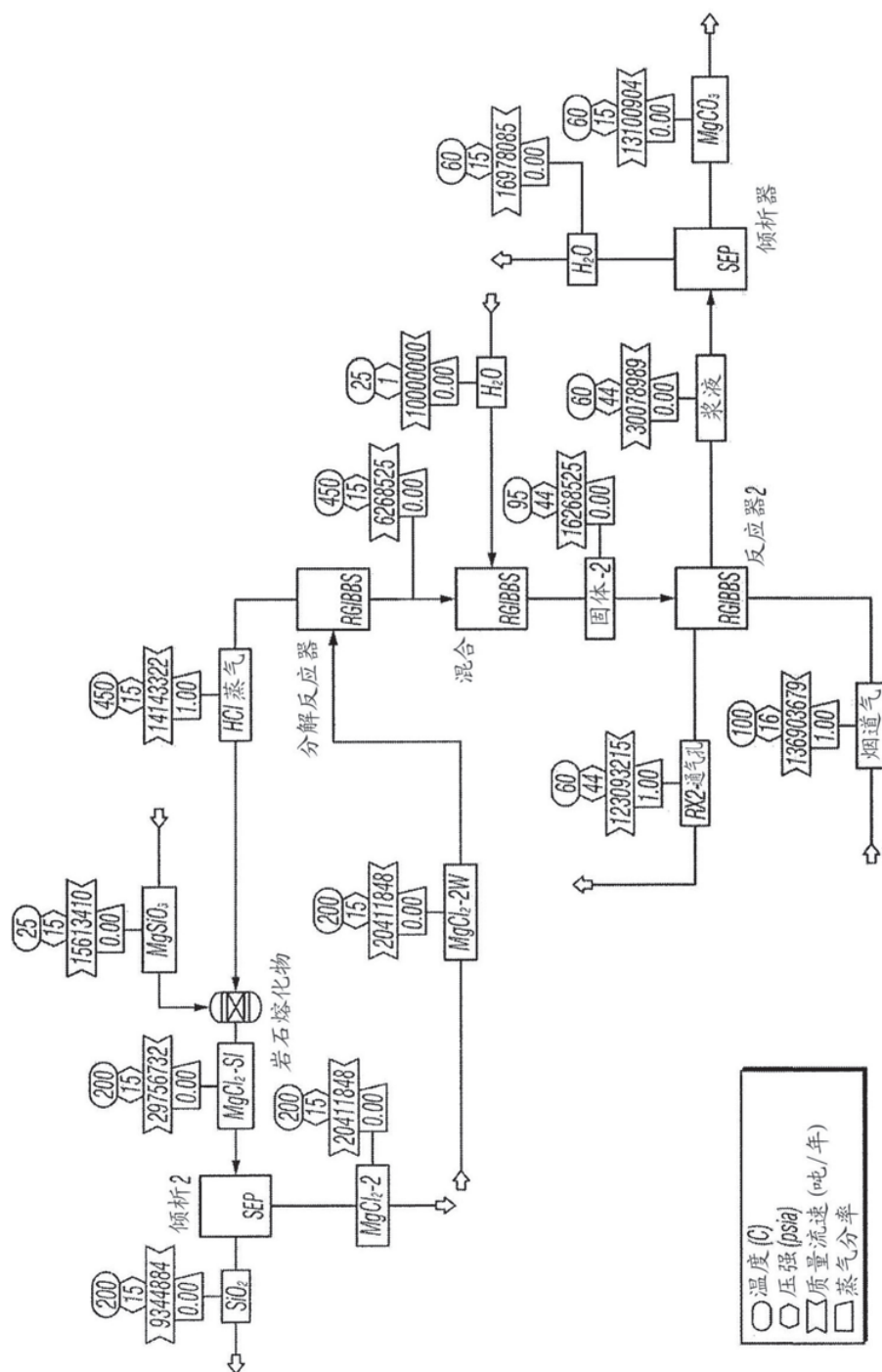


图 21

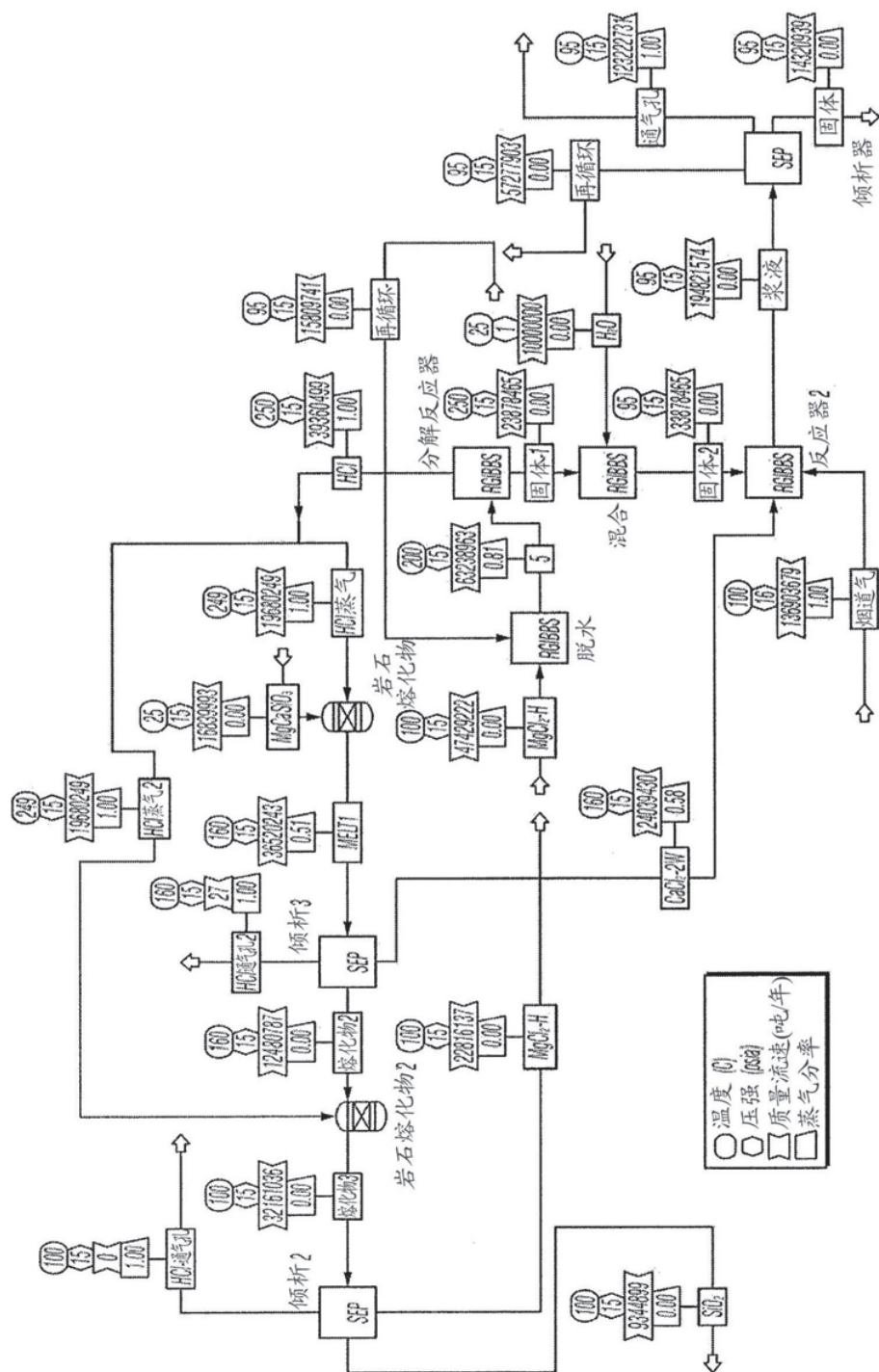


图 22

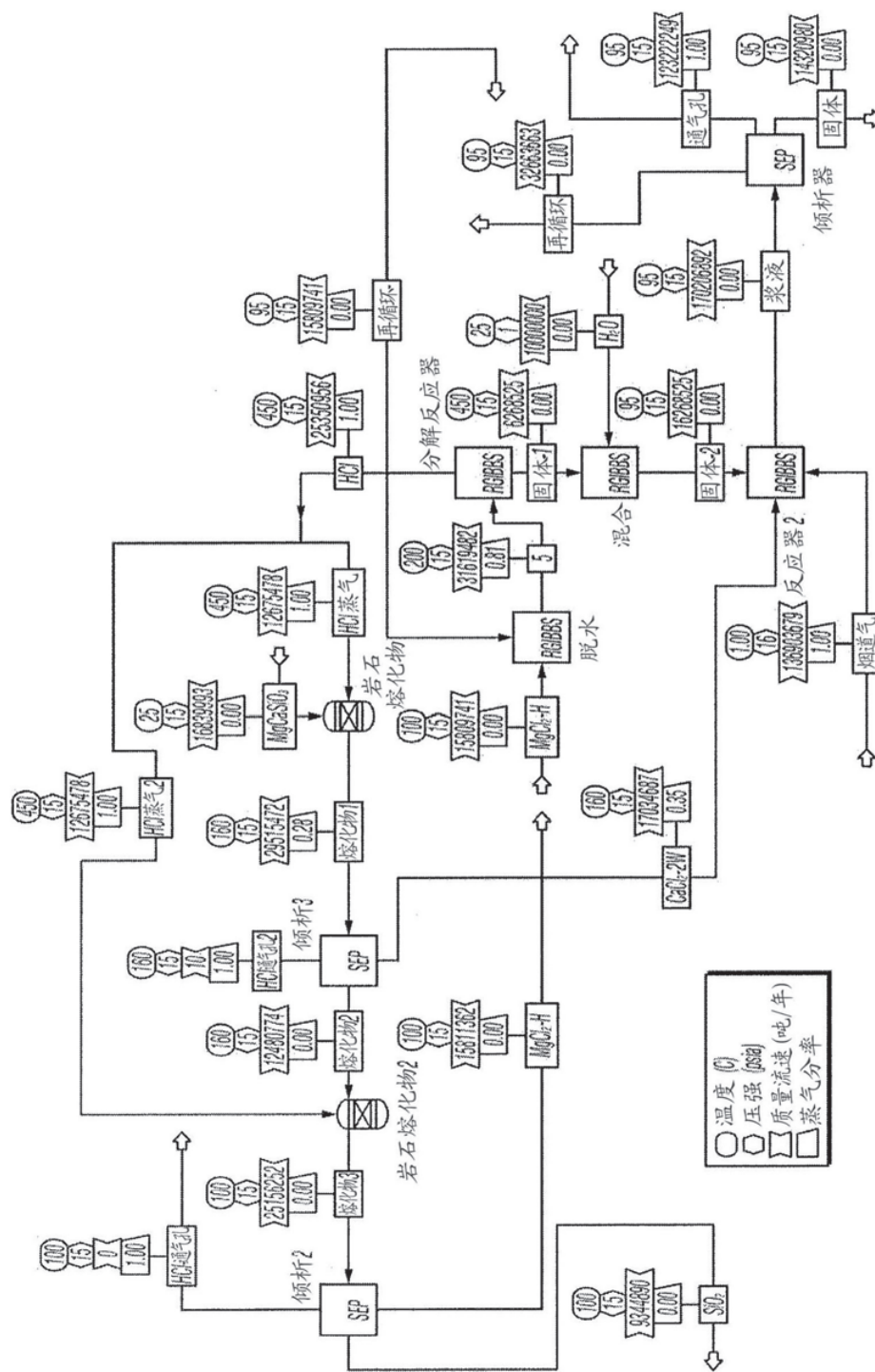


图 23

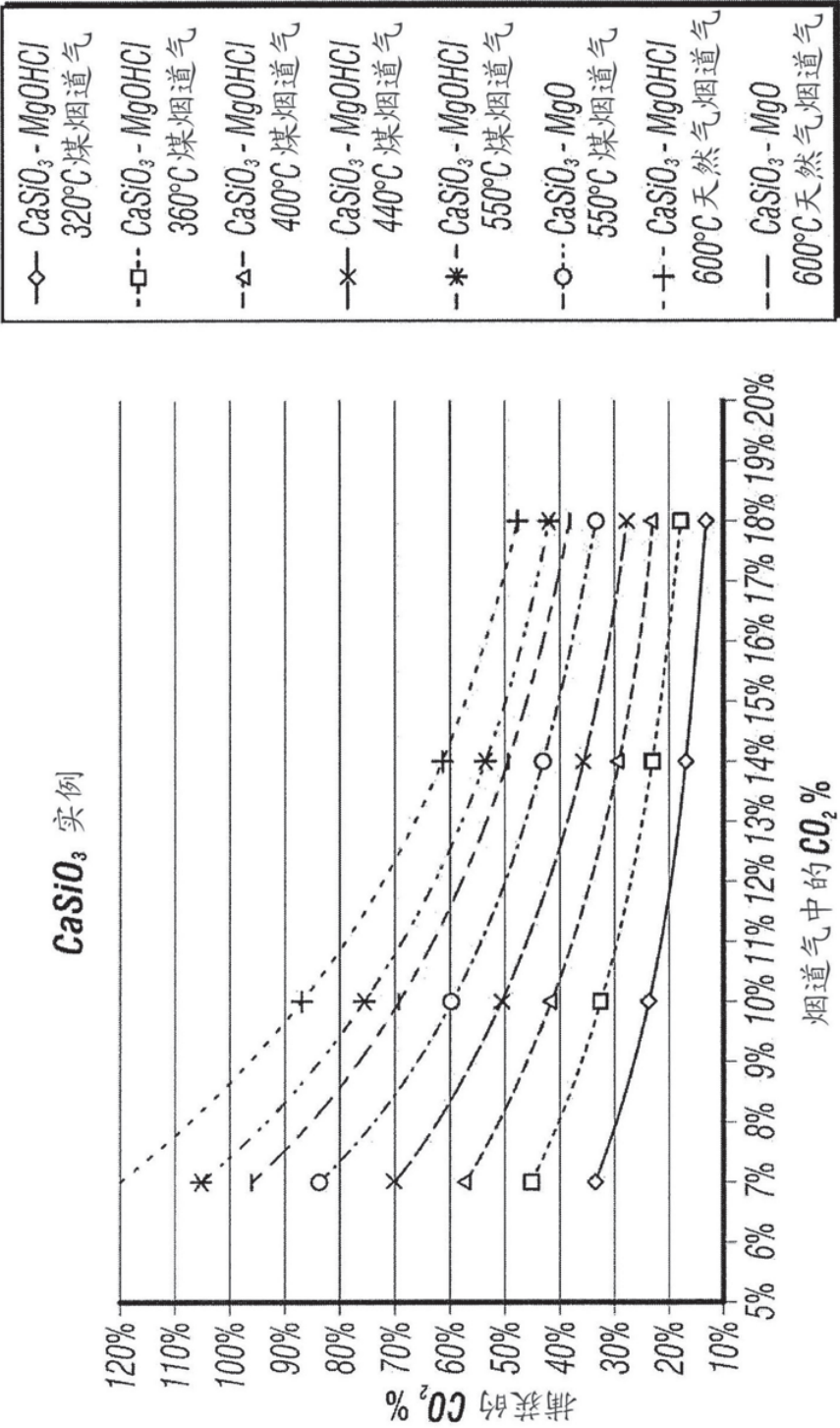


图 24

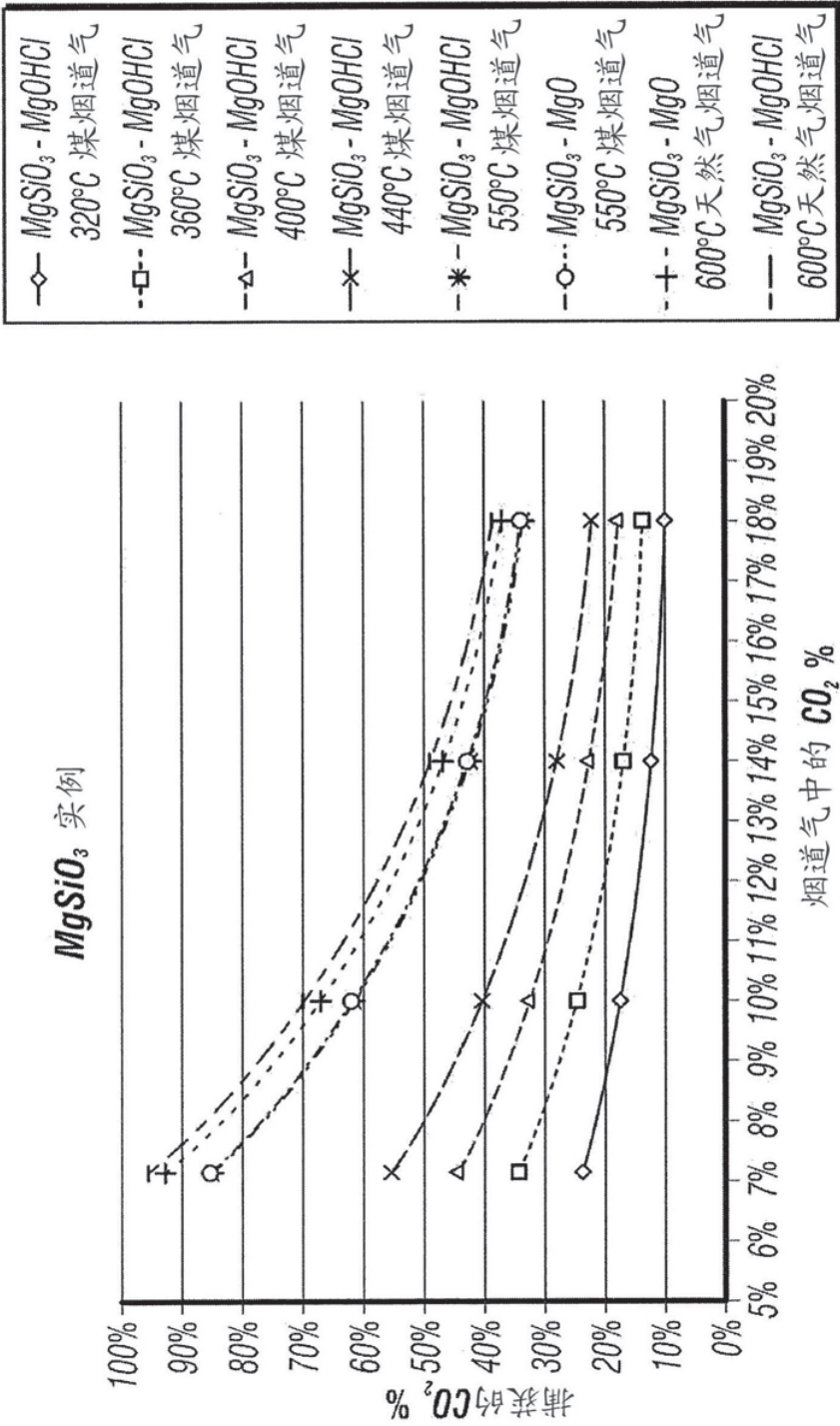


图 25

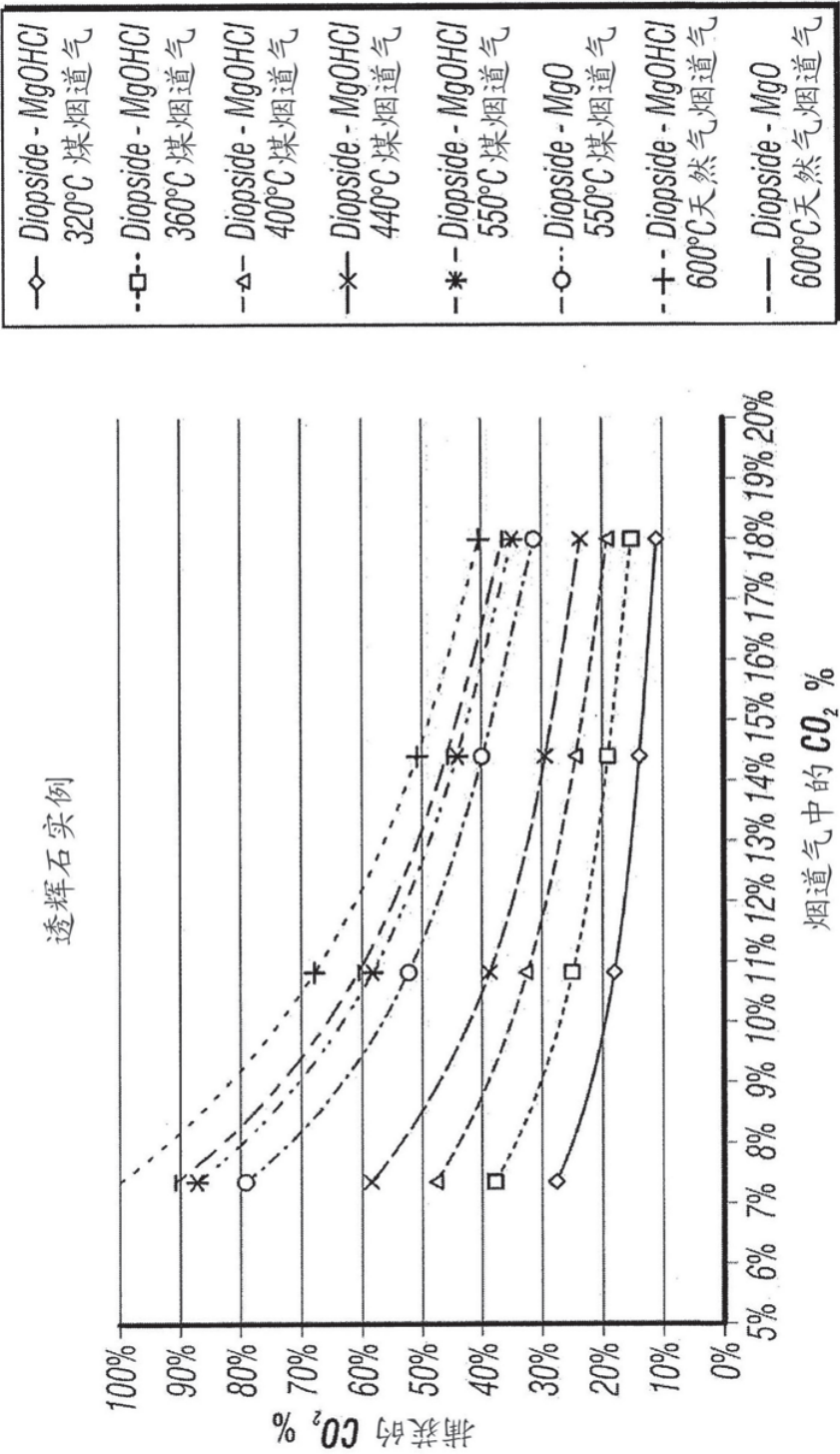


图 26

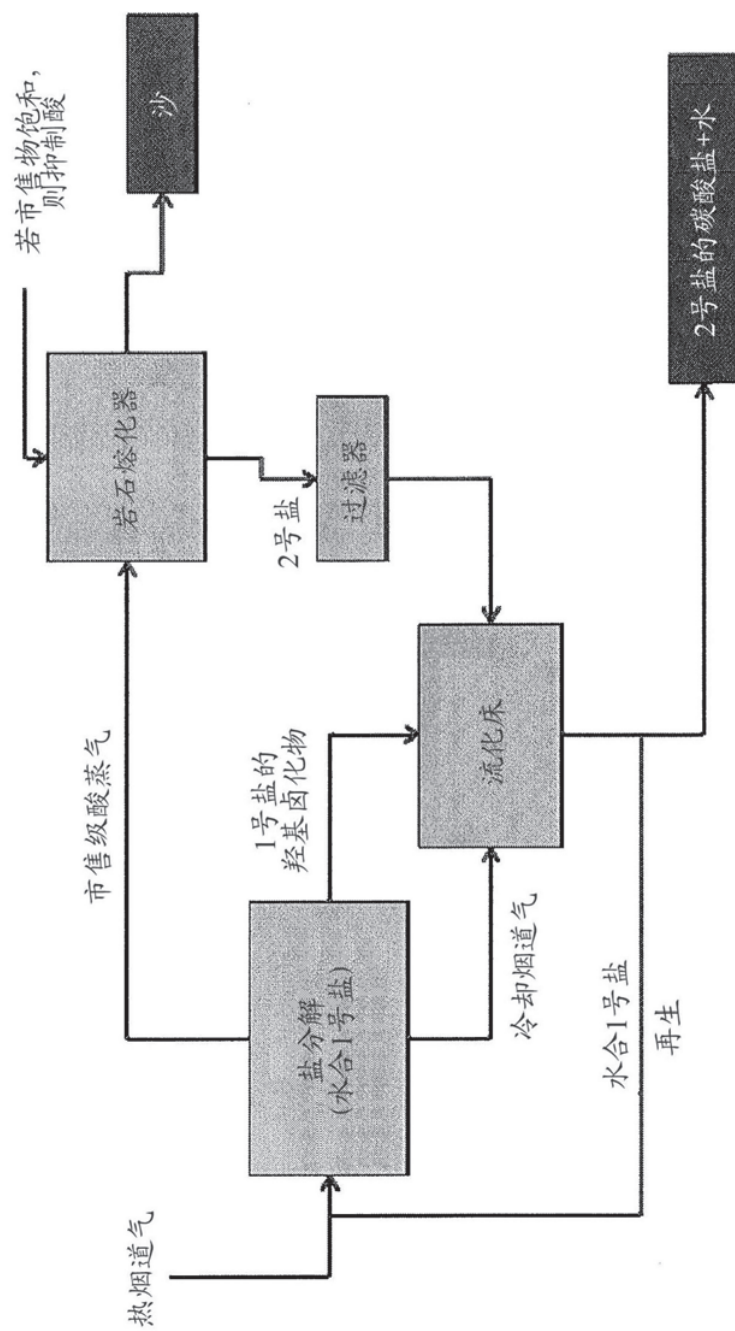


图 27

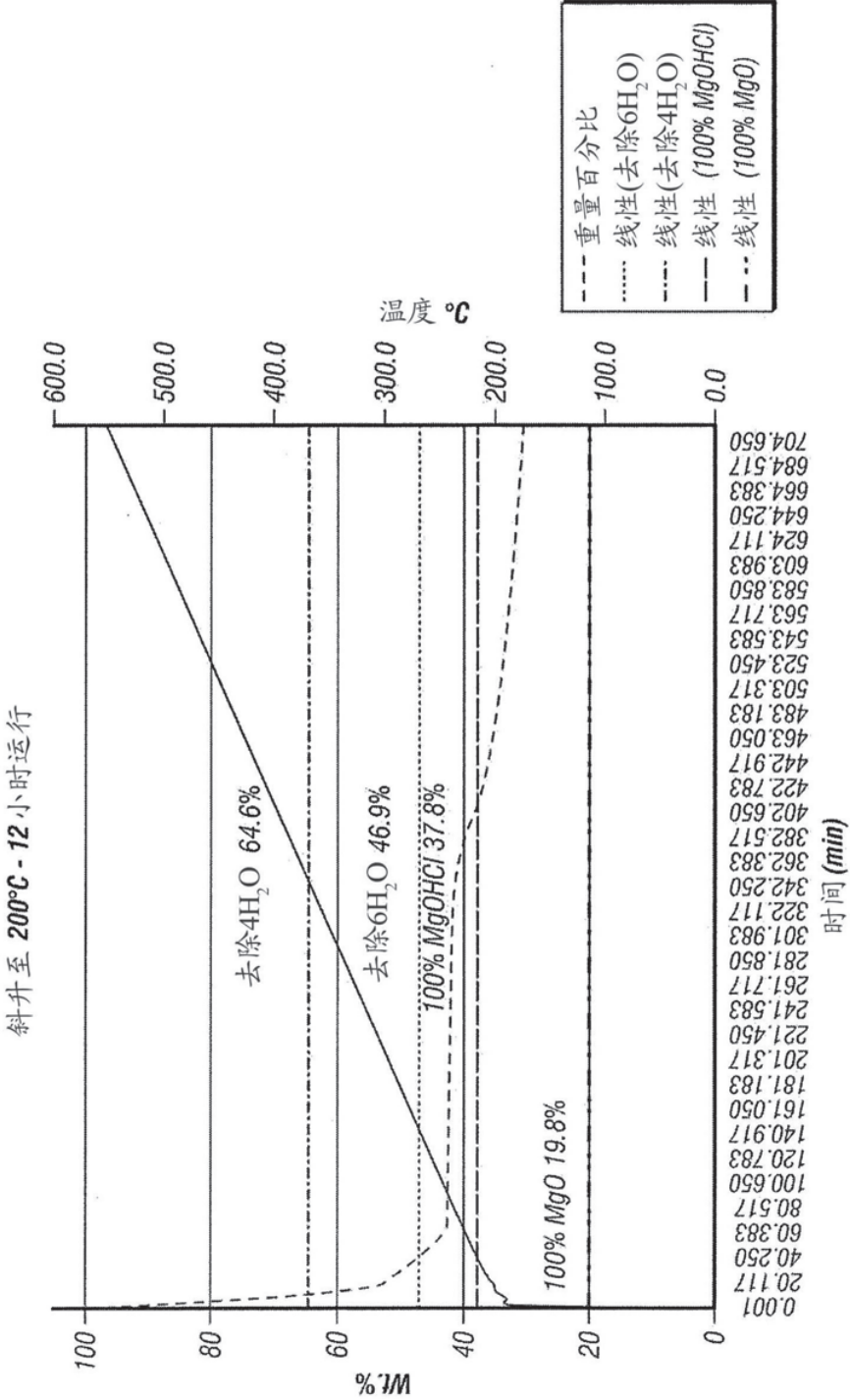


图 28

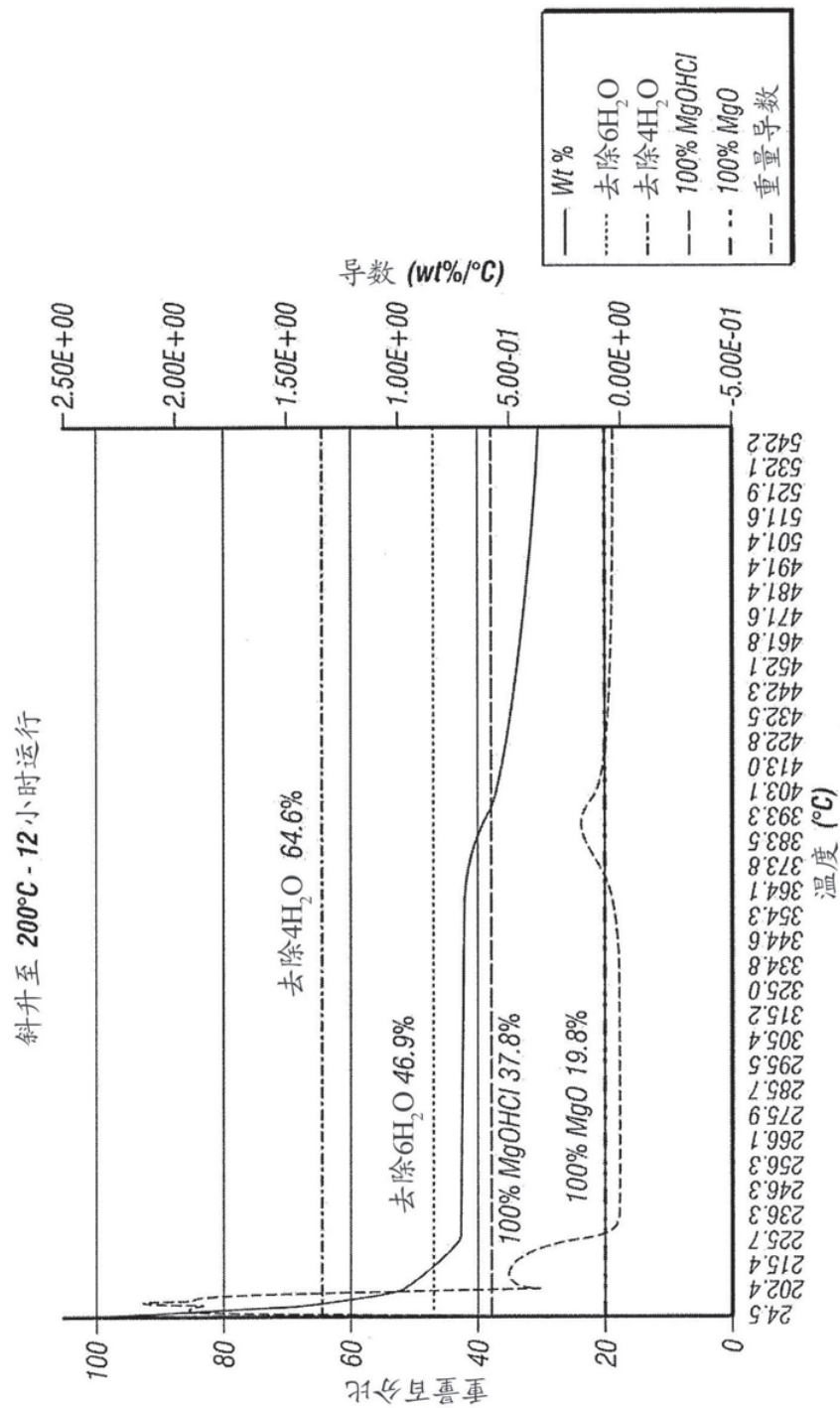


图 29

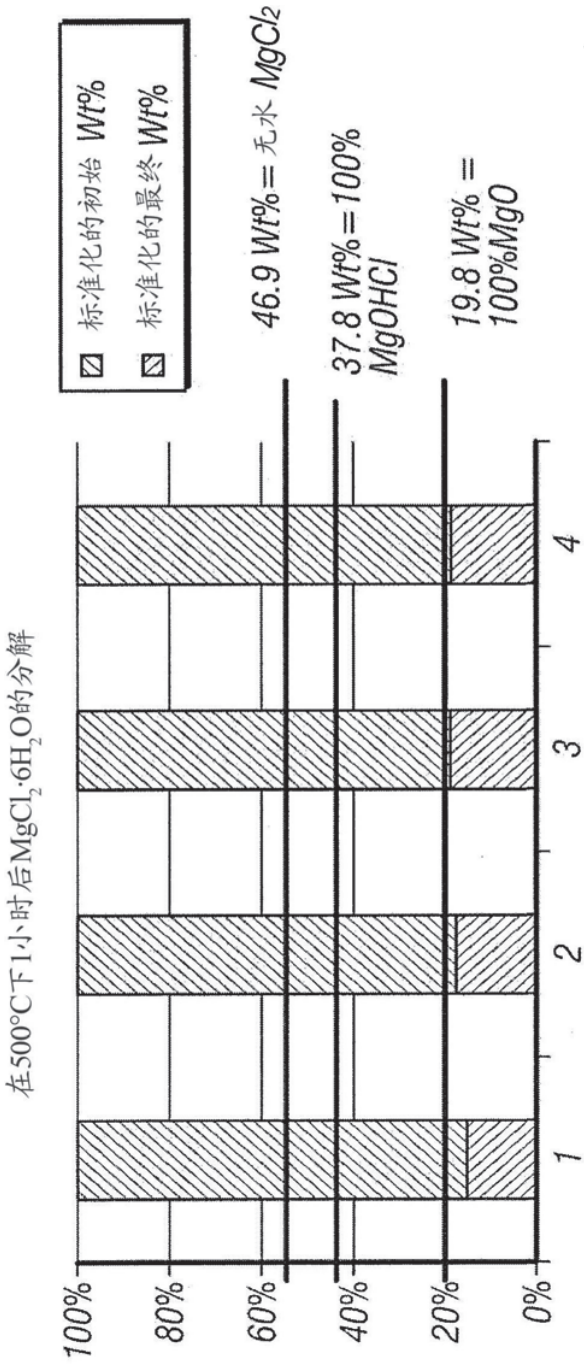


图 30

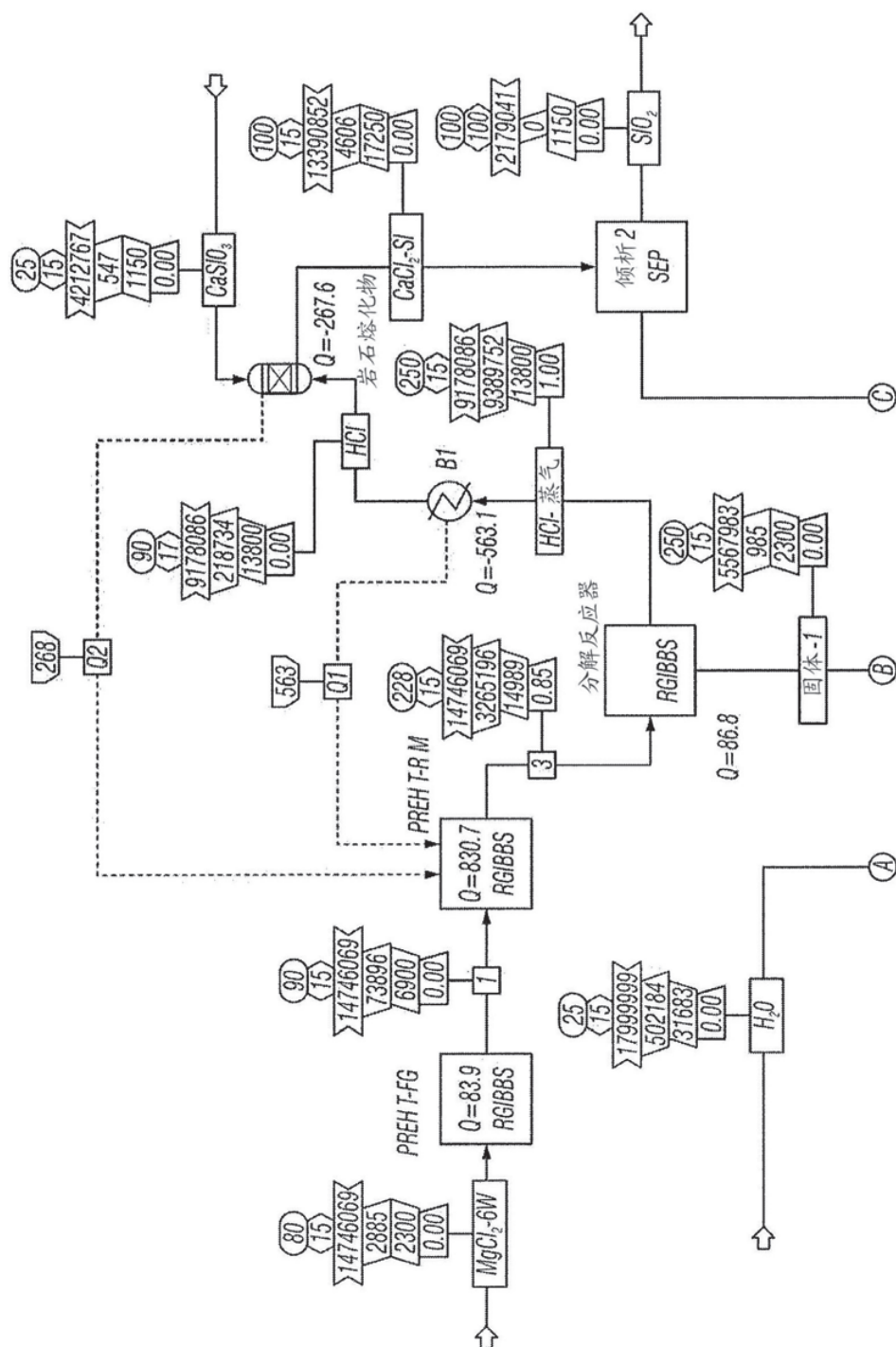


图 31

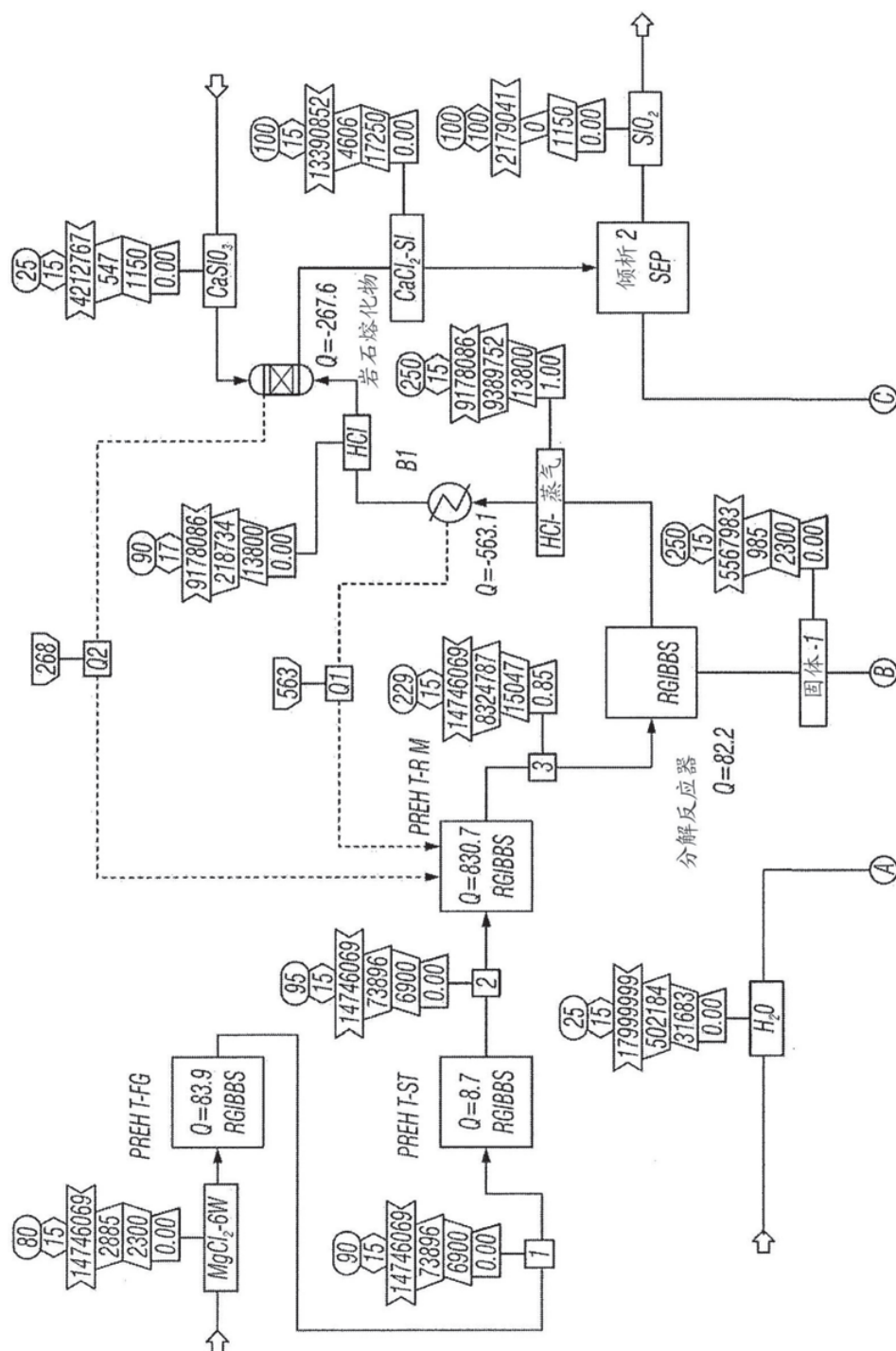


图 32

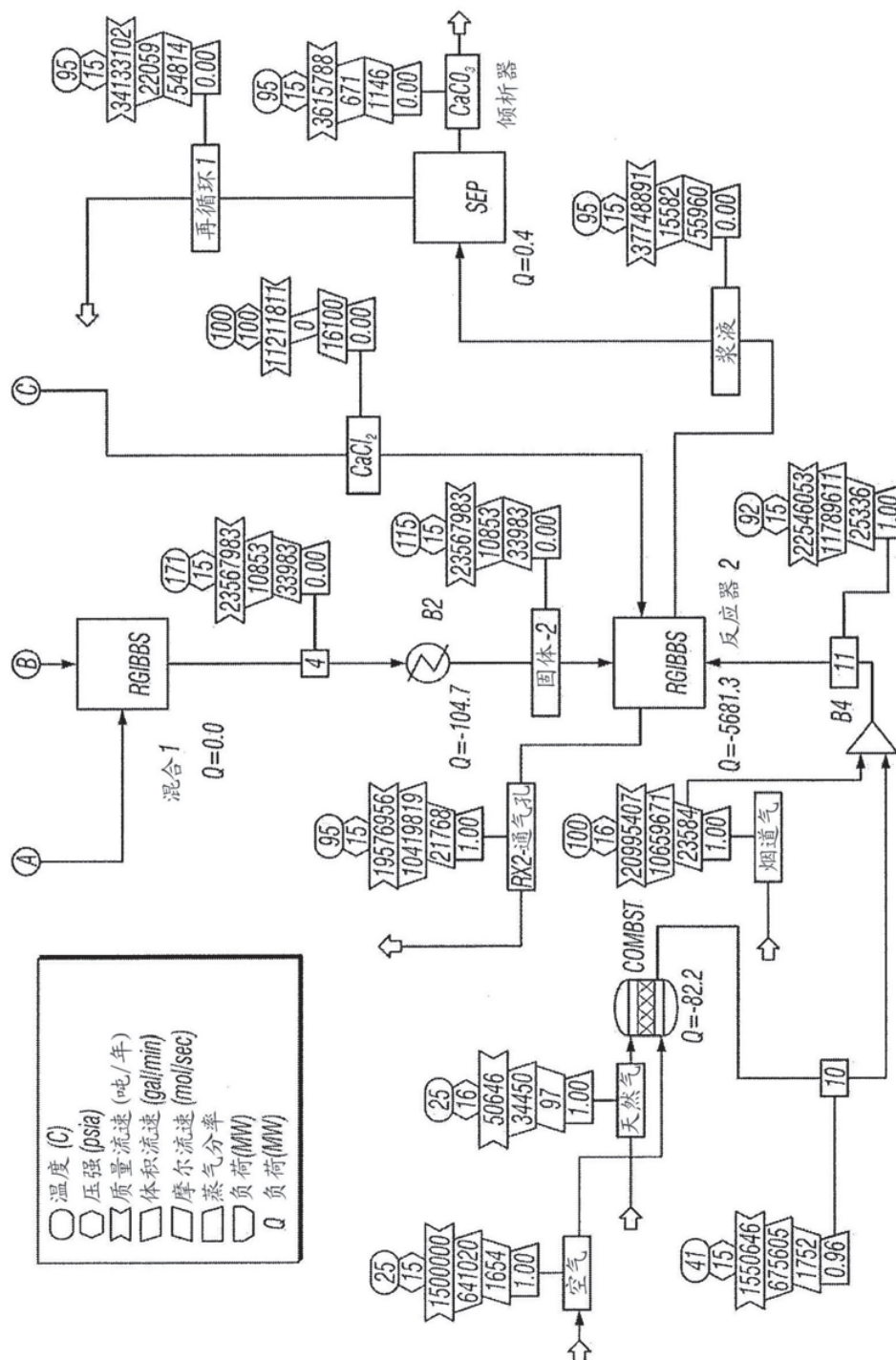


图 32(续)

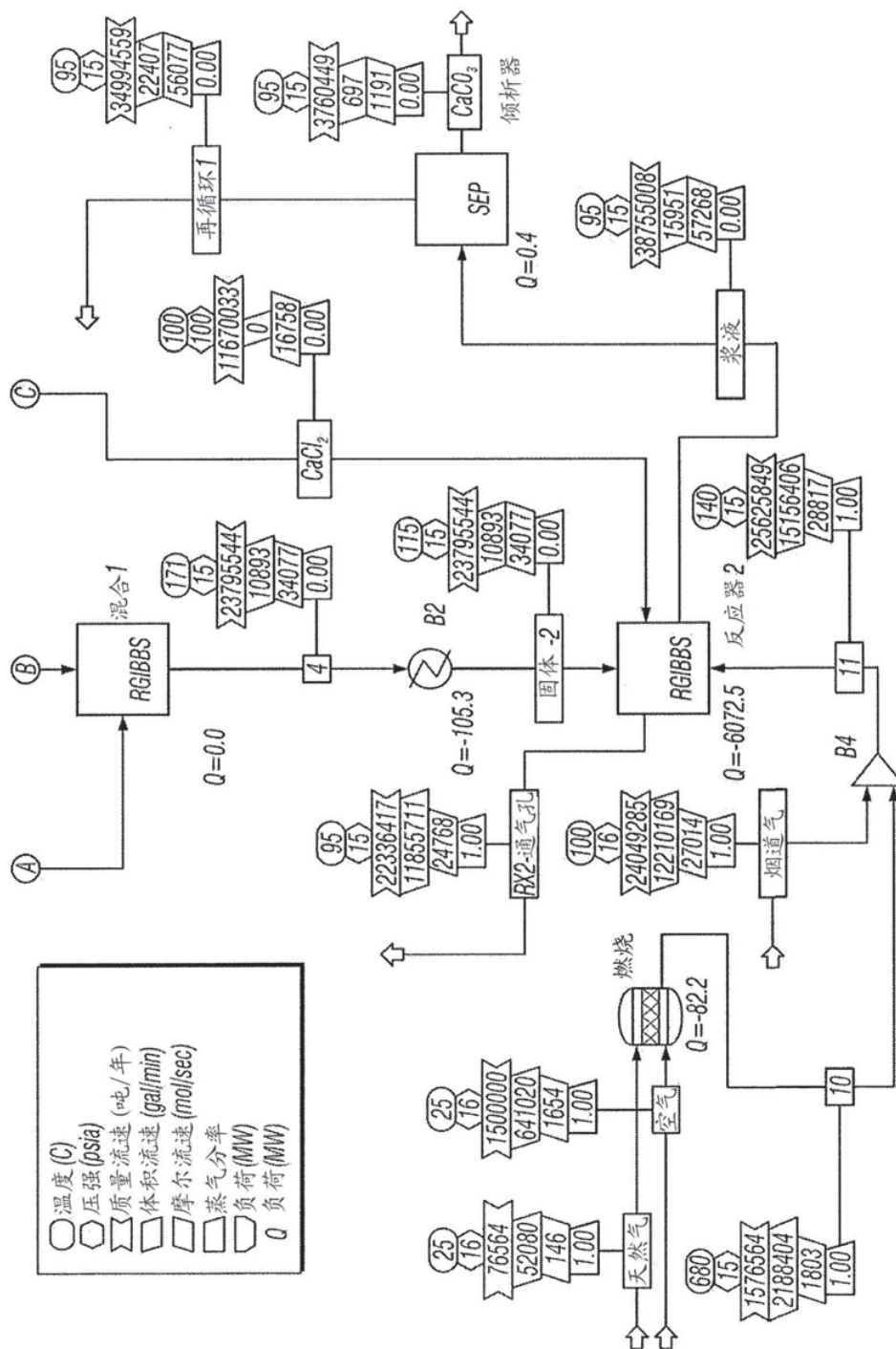


图 33(续)

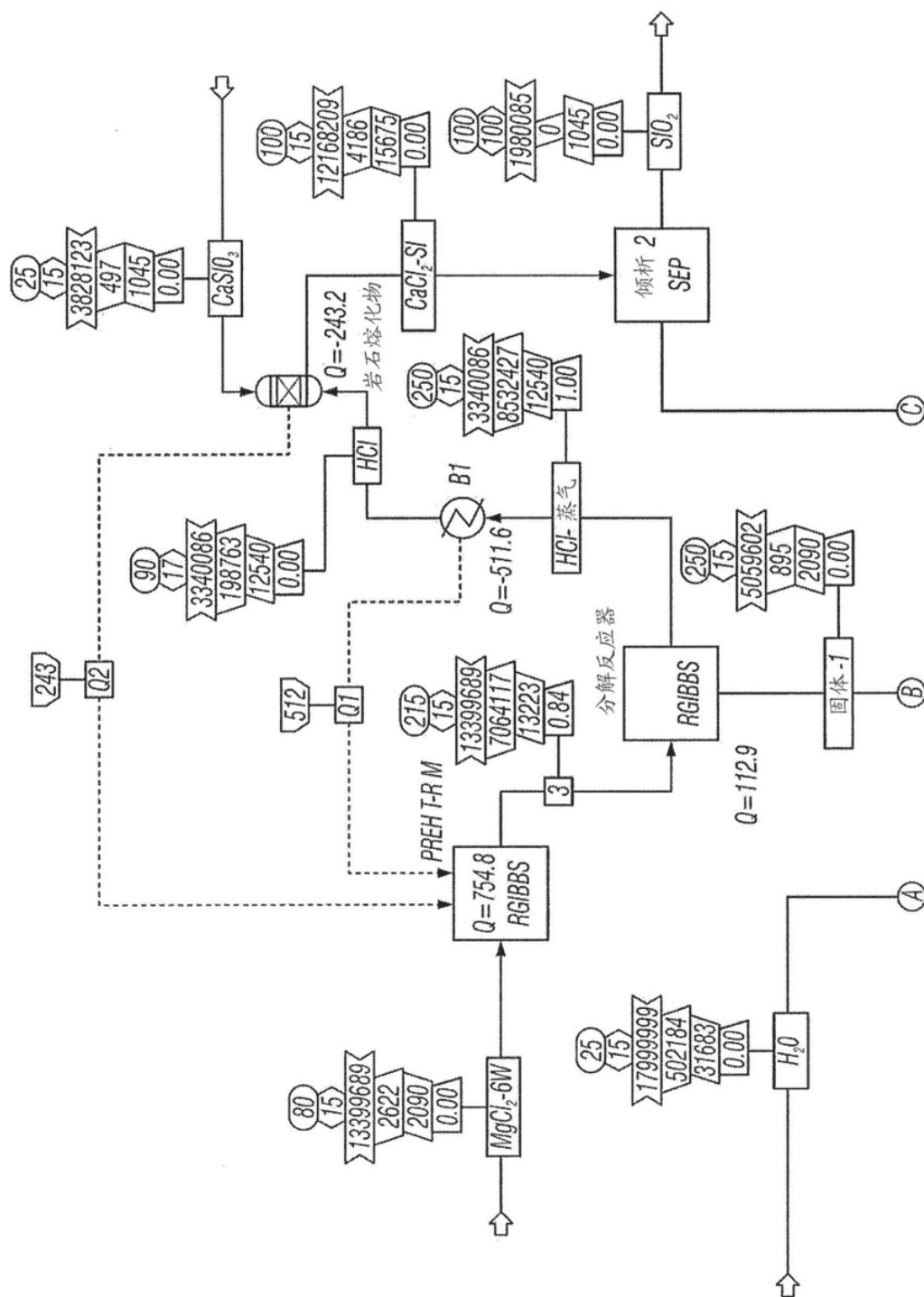


图 34

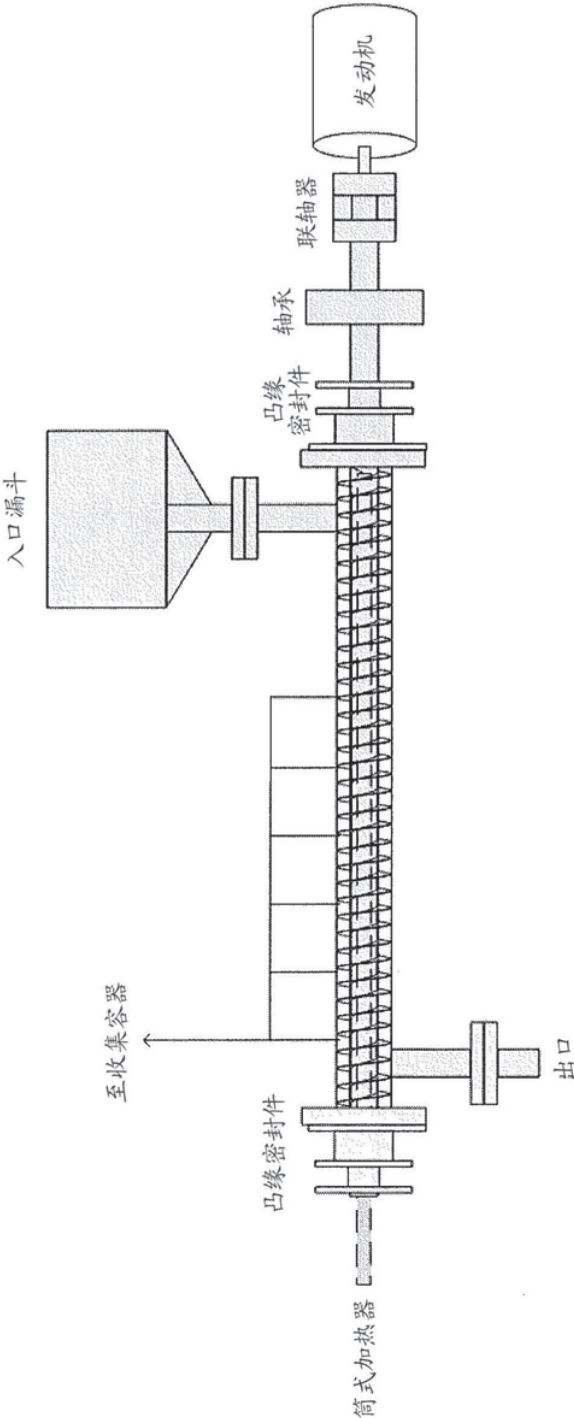


图 35

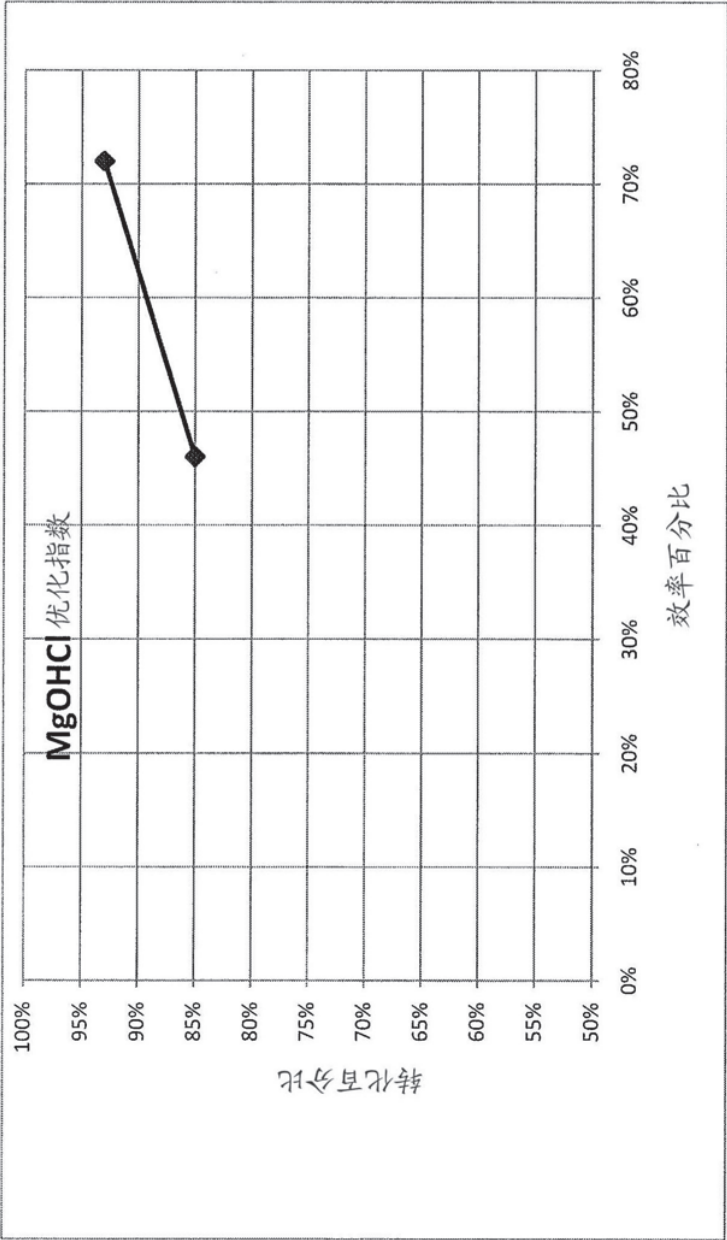


图 36

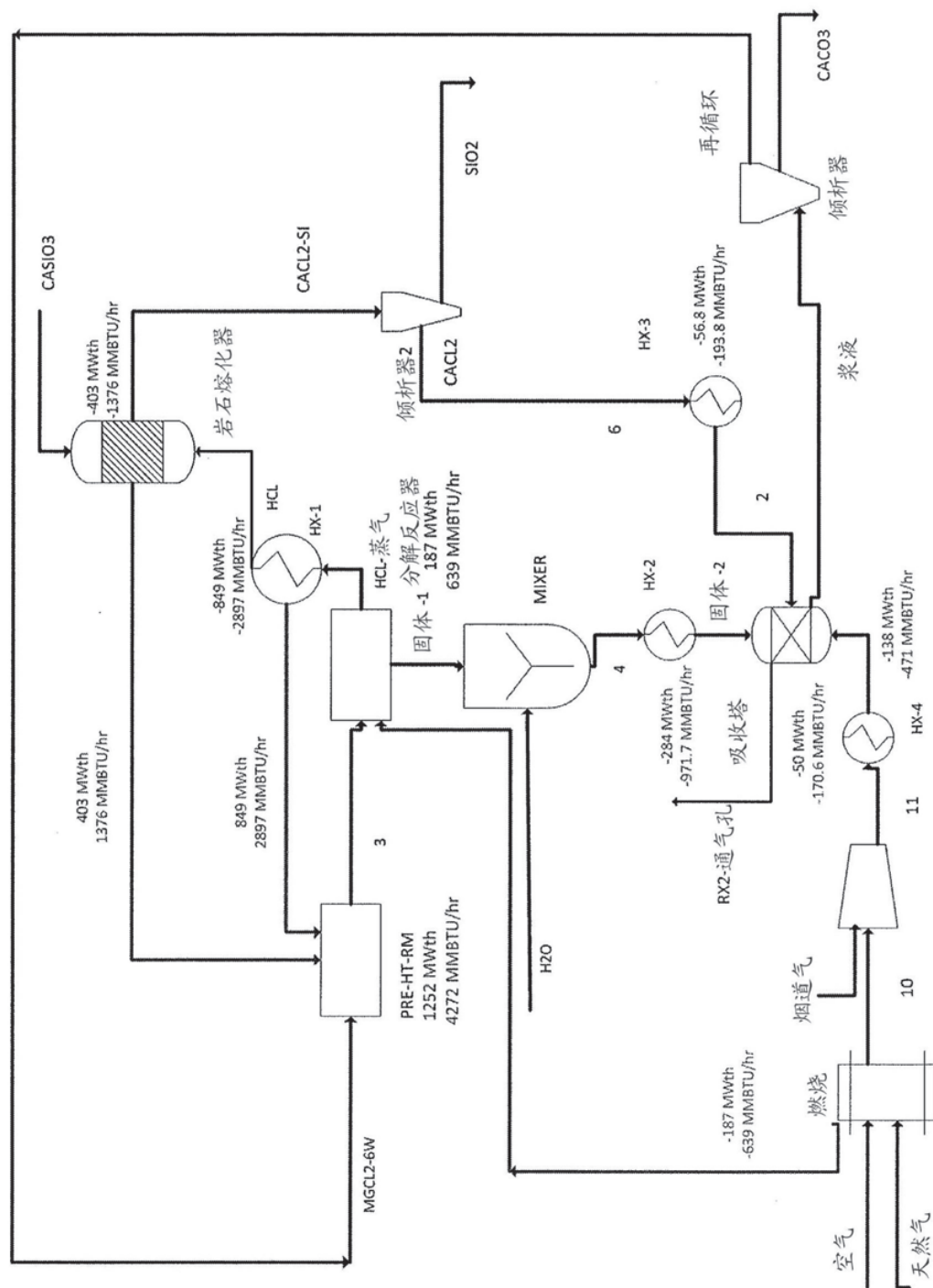


图 37

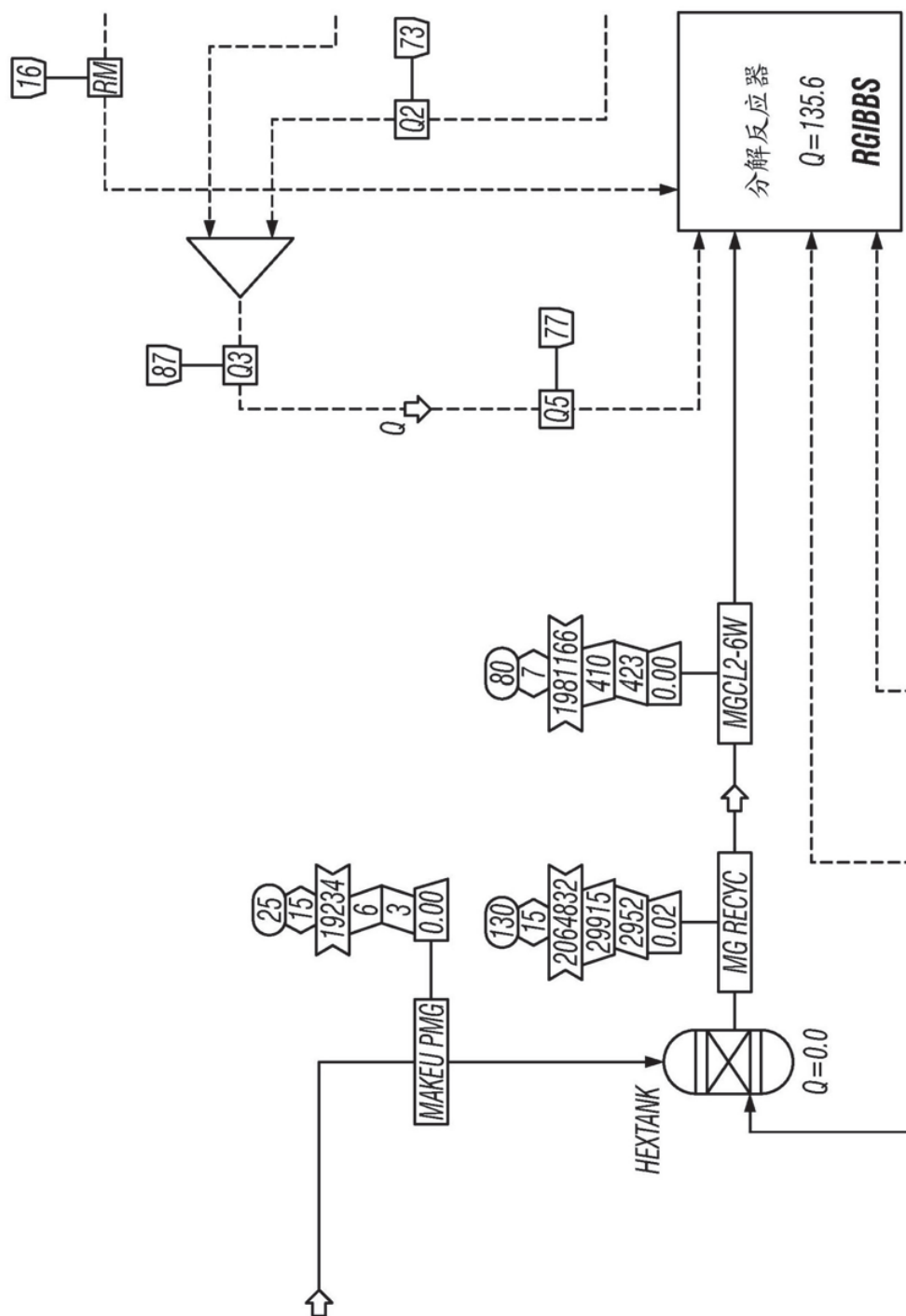


图 38B

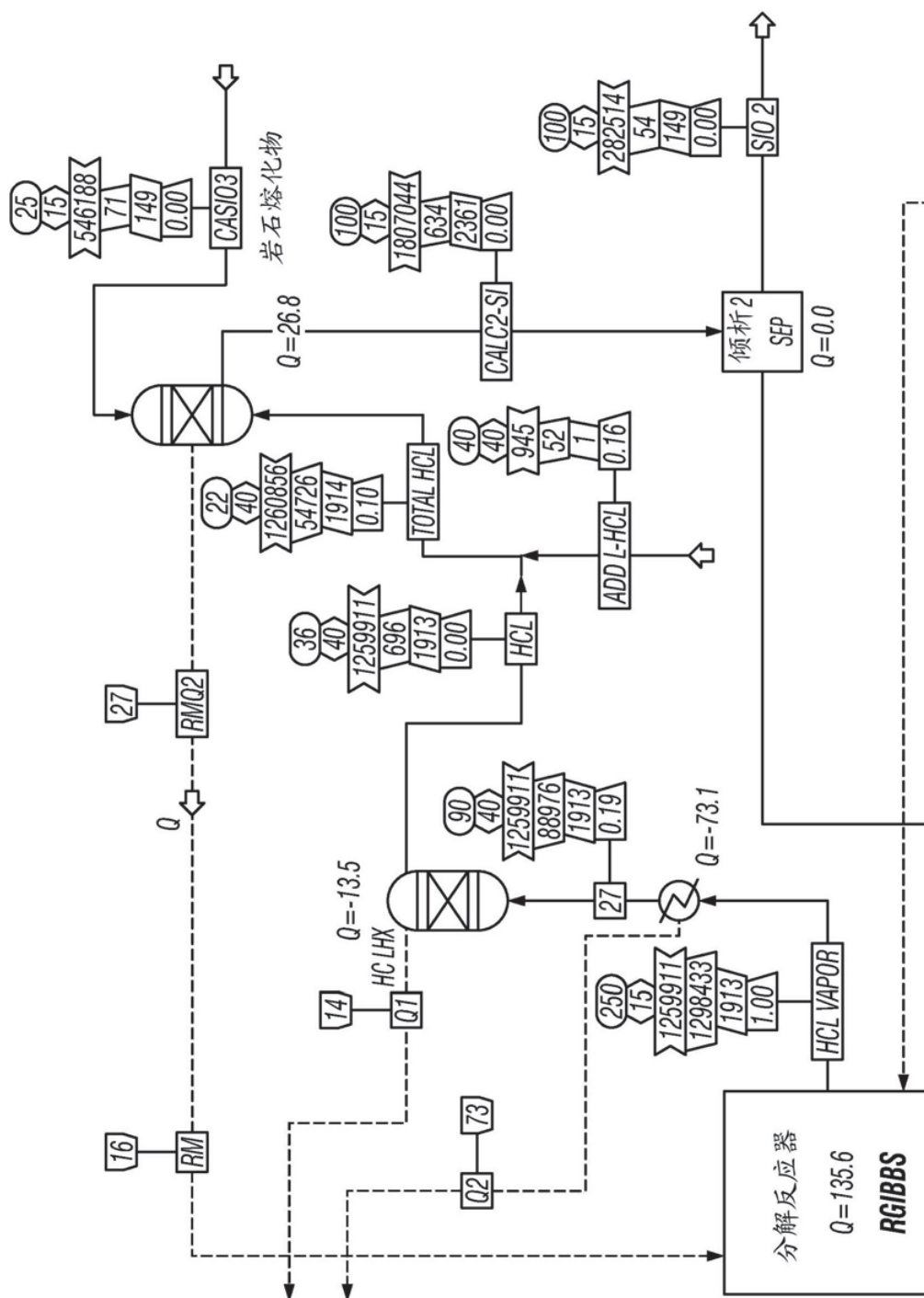


图 38C

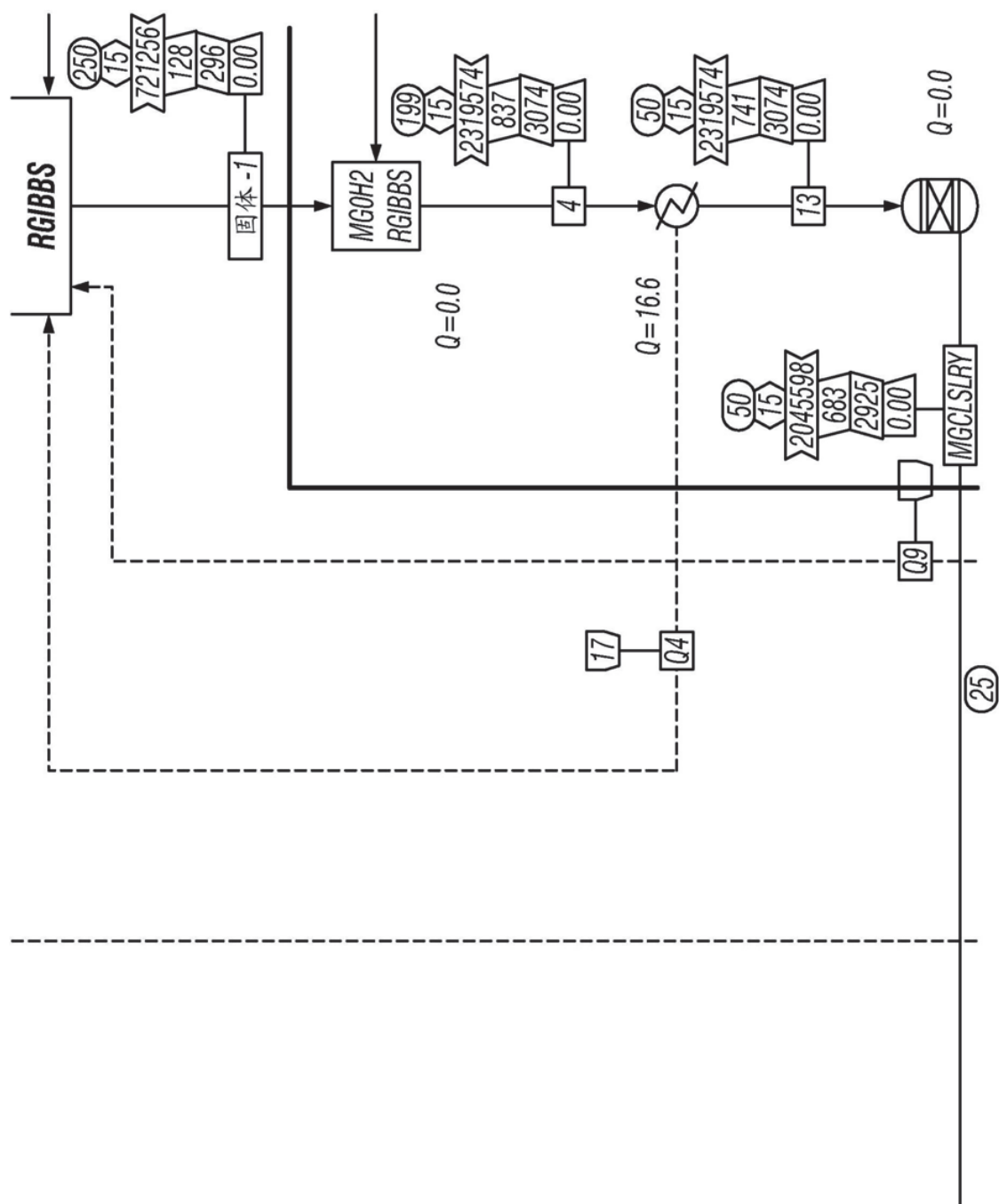


图 38D

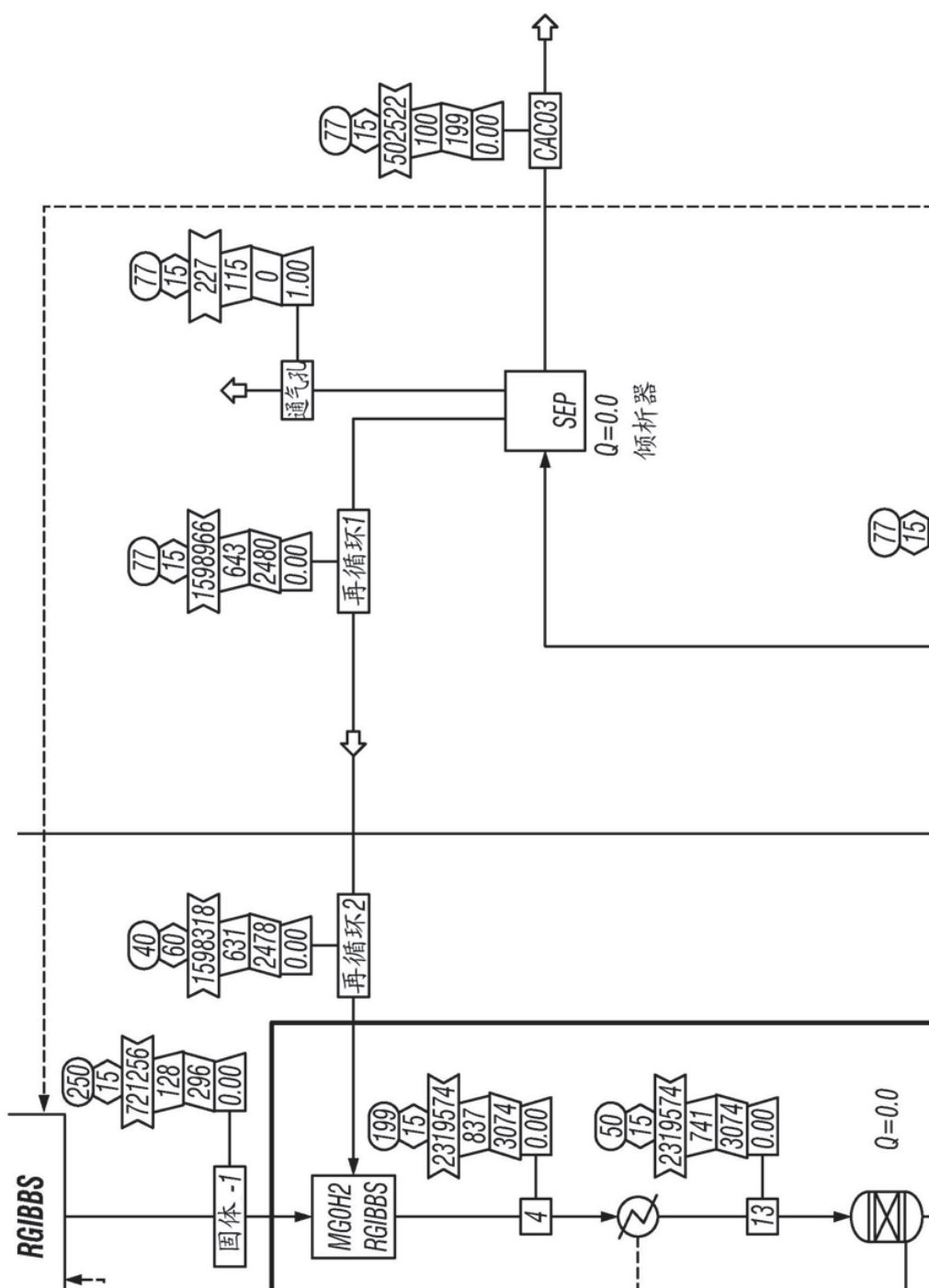


图 38E

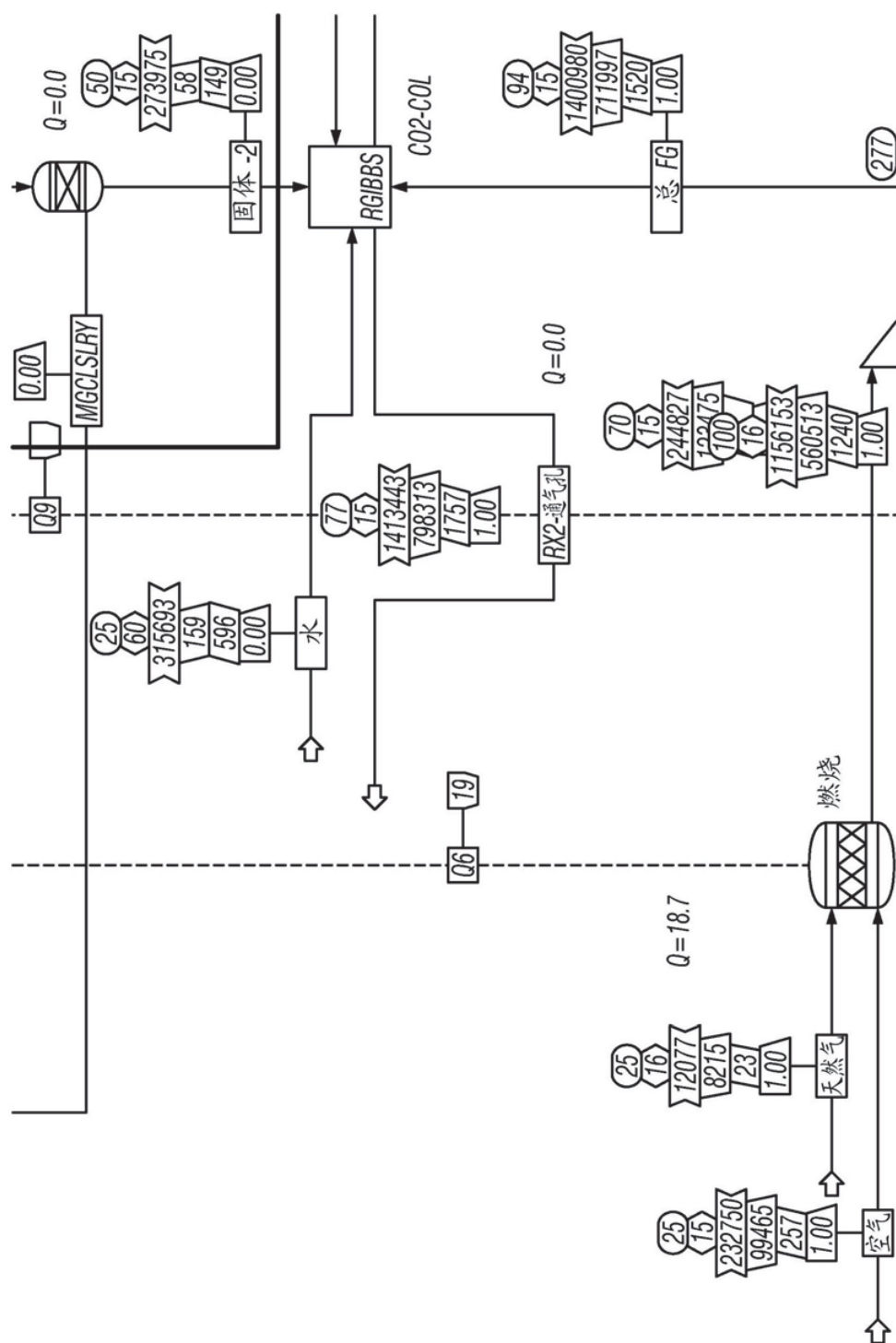


图 38F

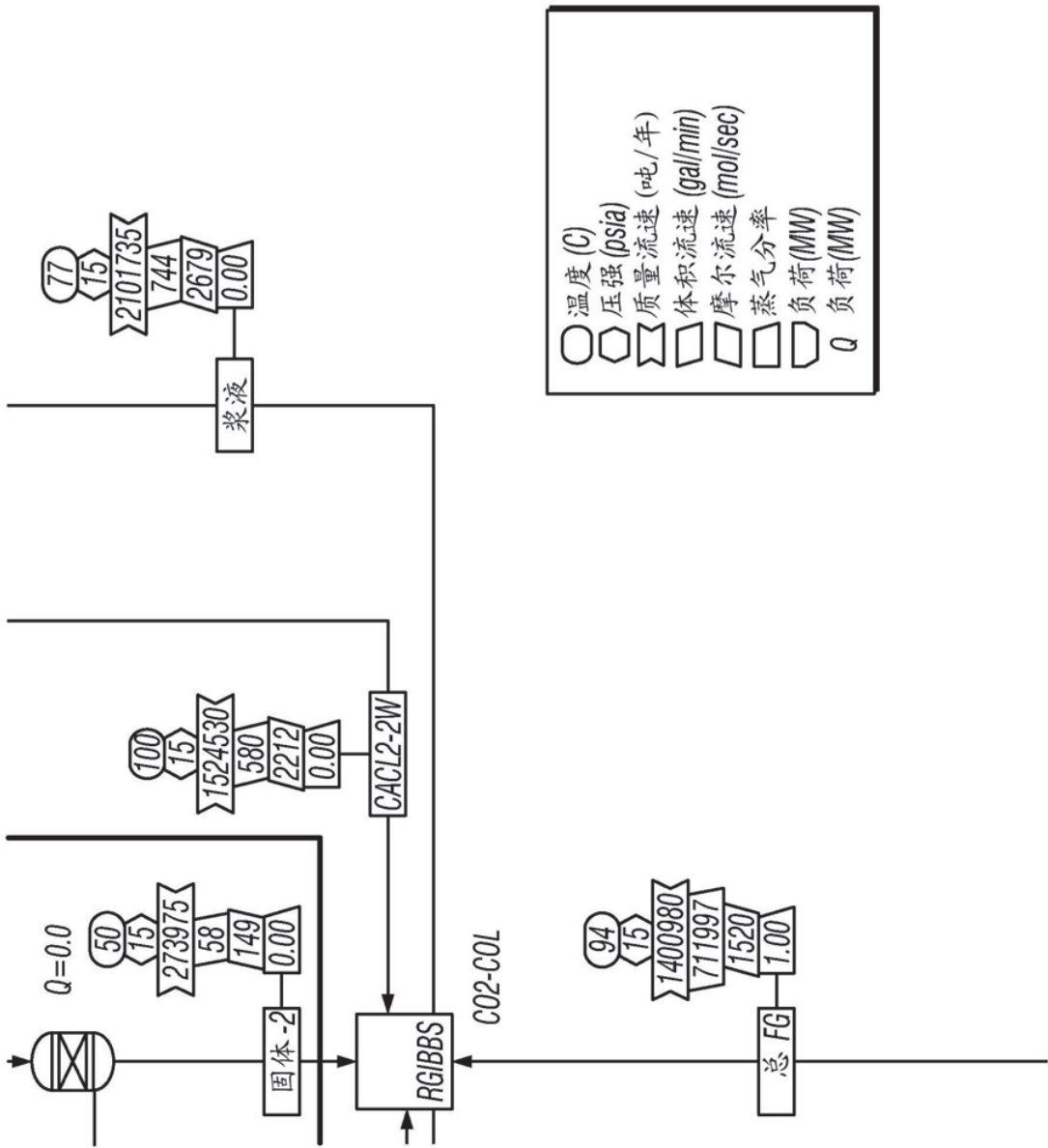


图 38G

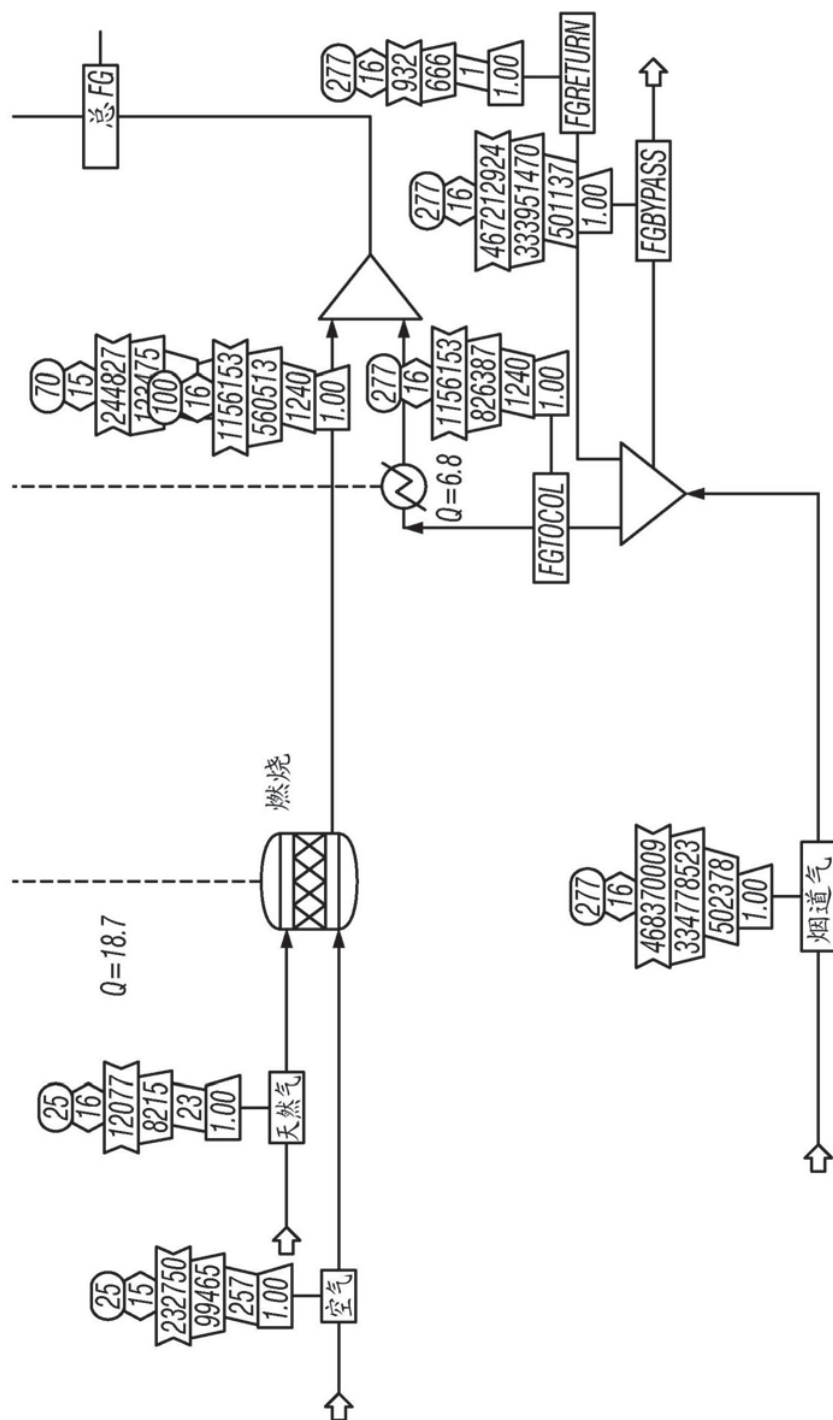


图 38H

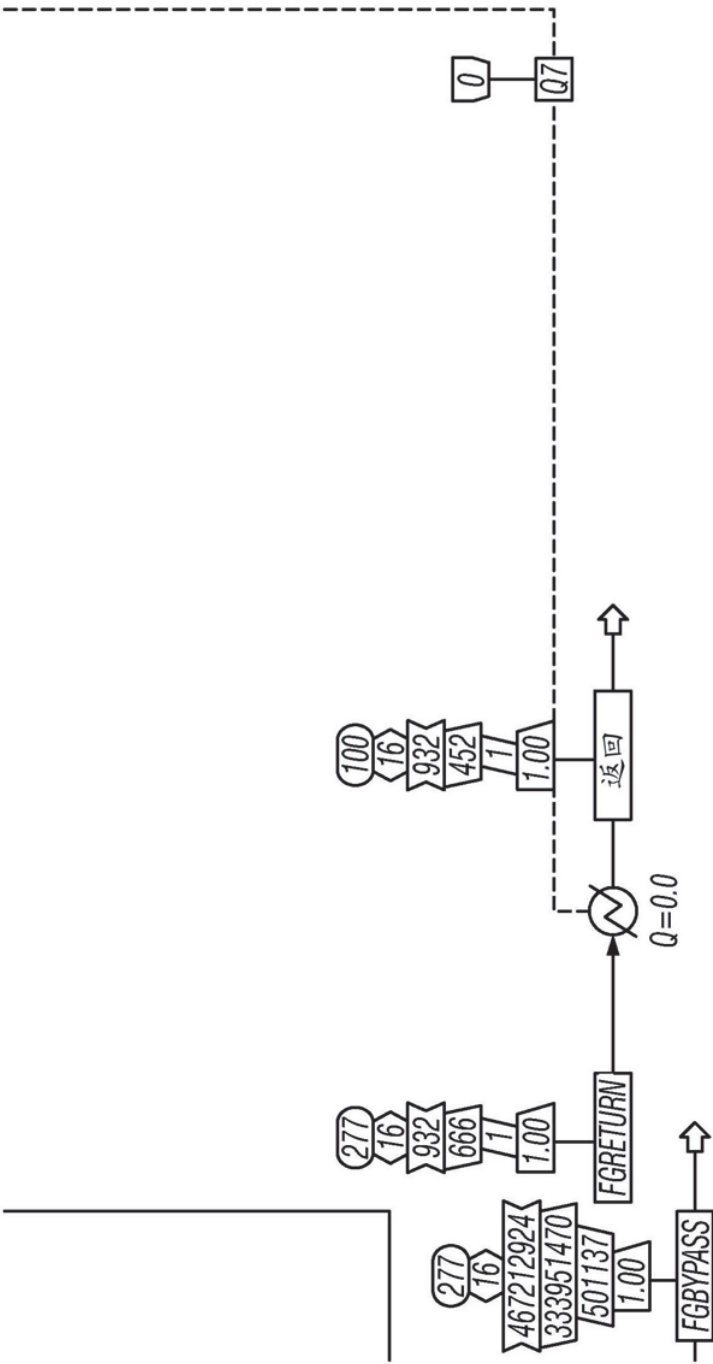


图 38I

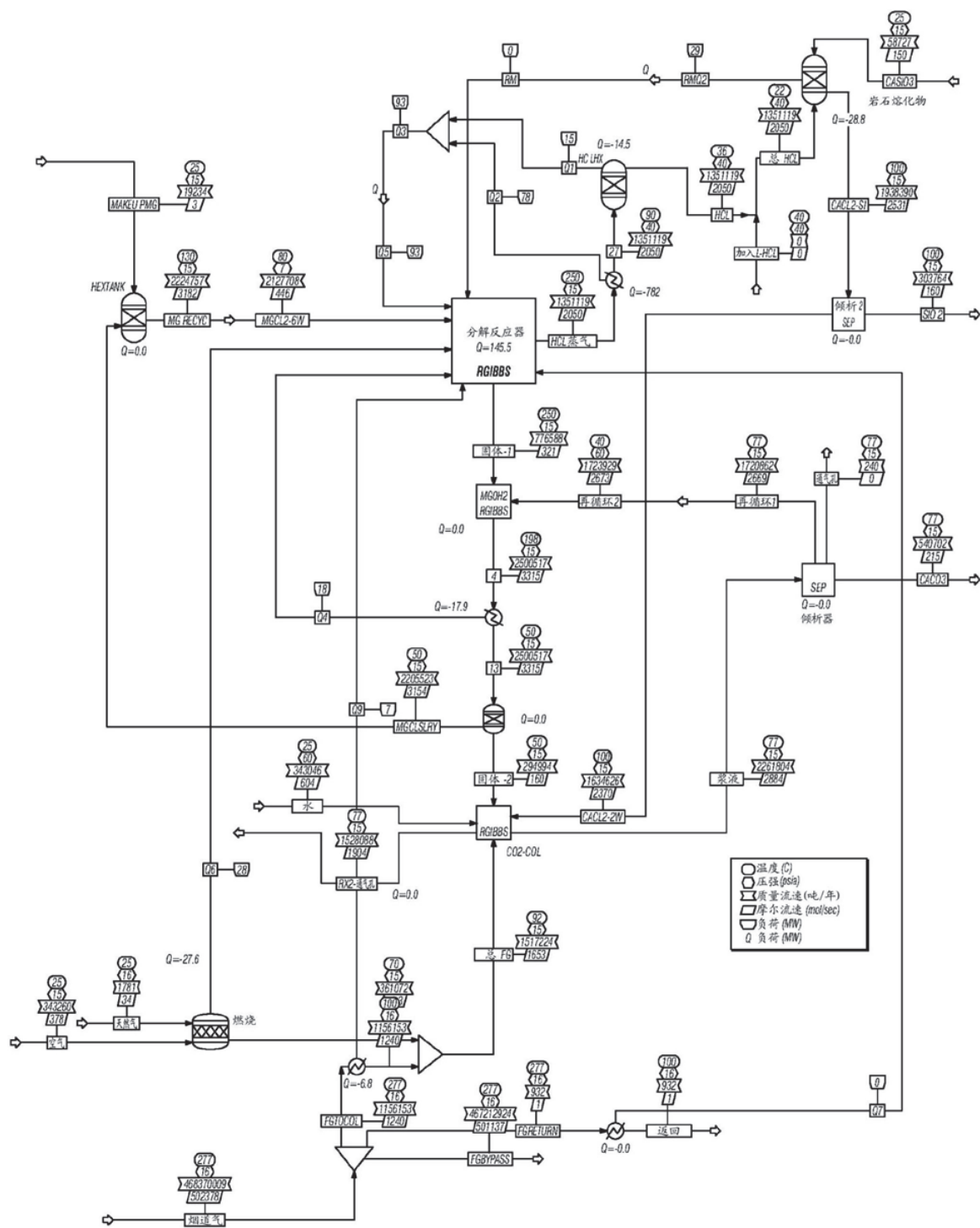


图 39A

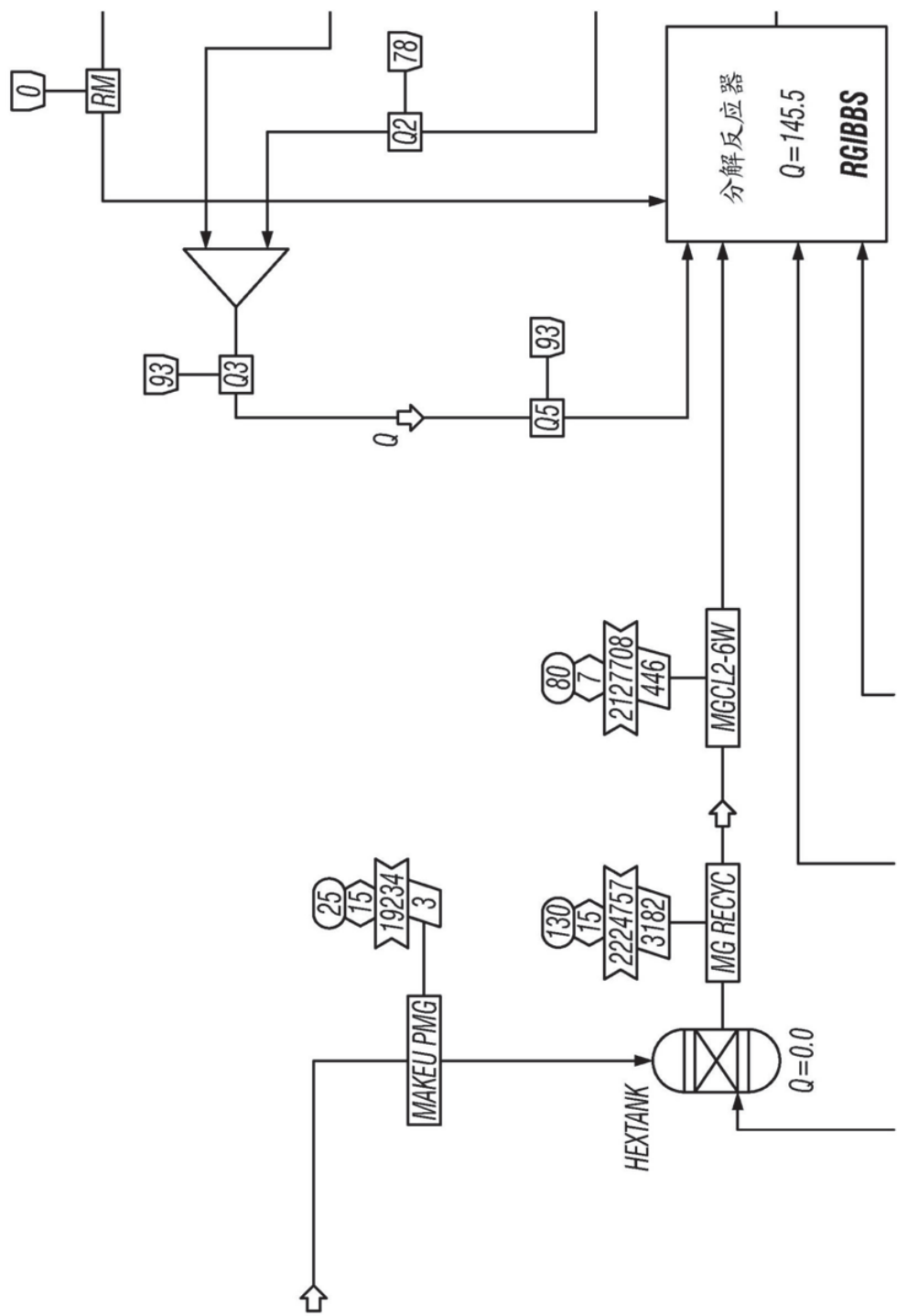


图 39B

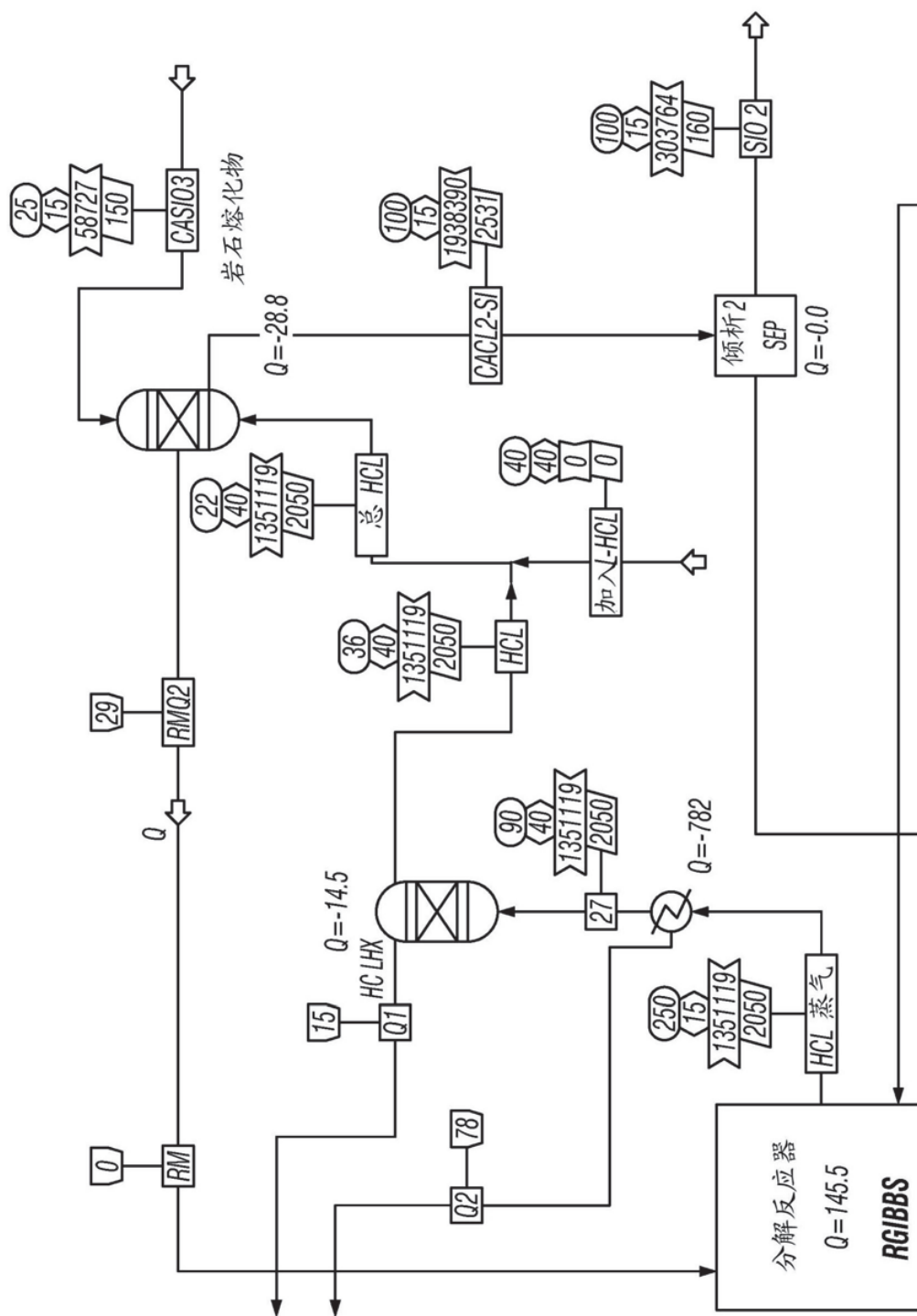


图 39C

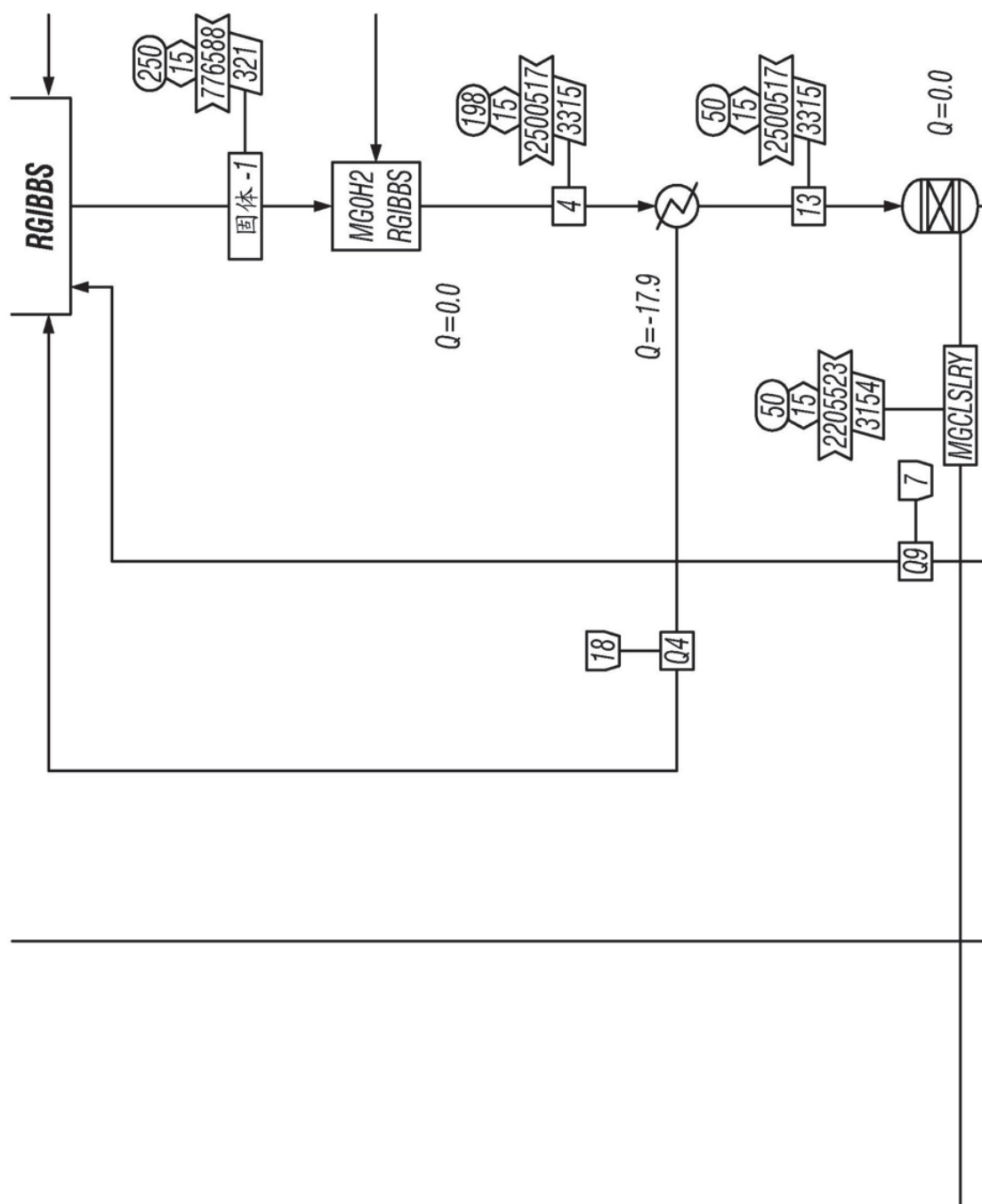


图 39D

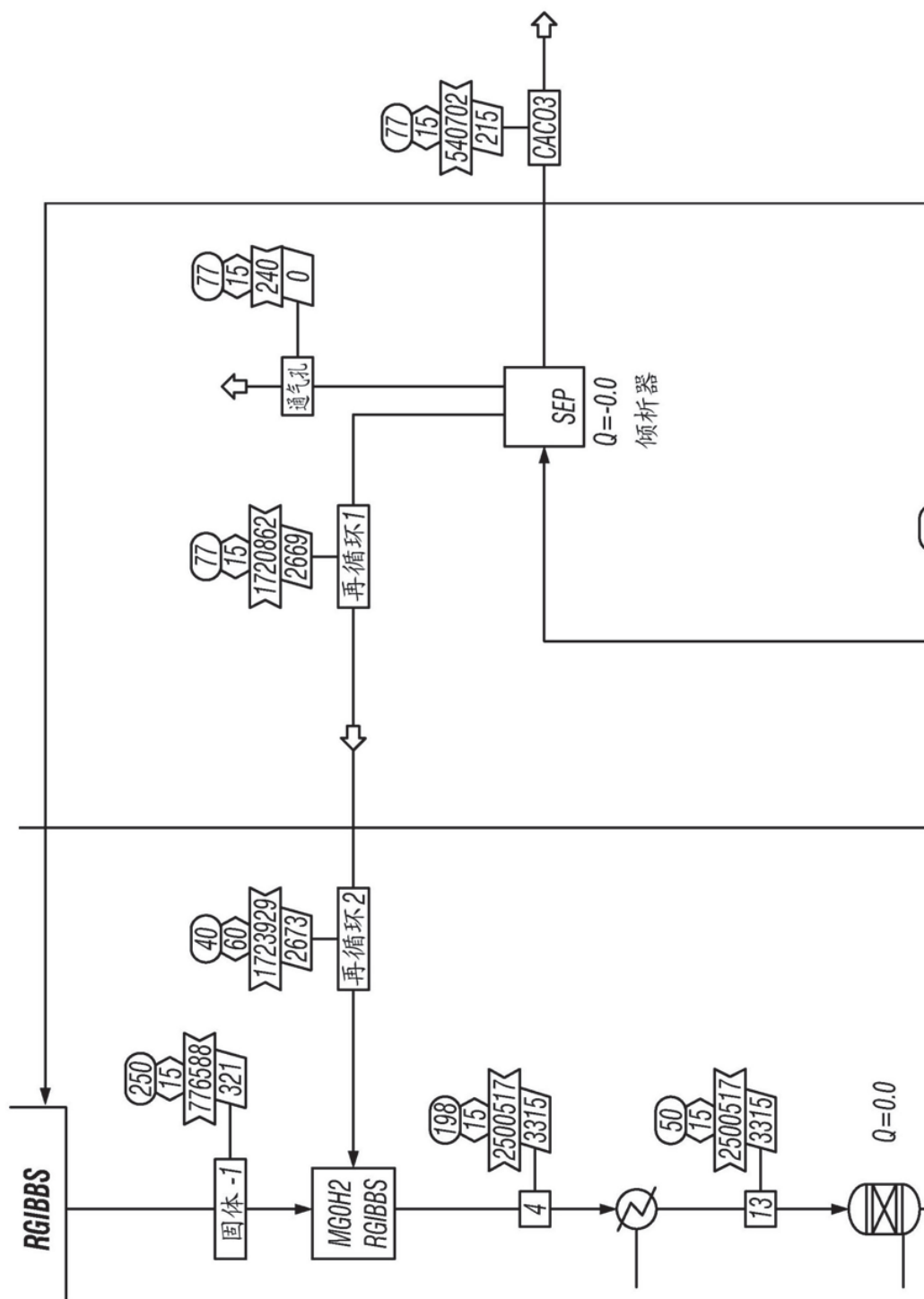


图 39E

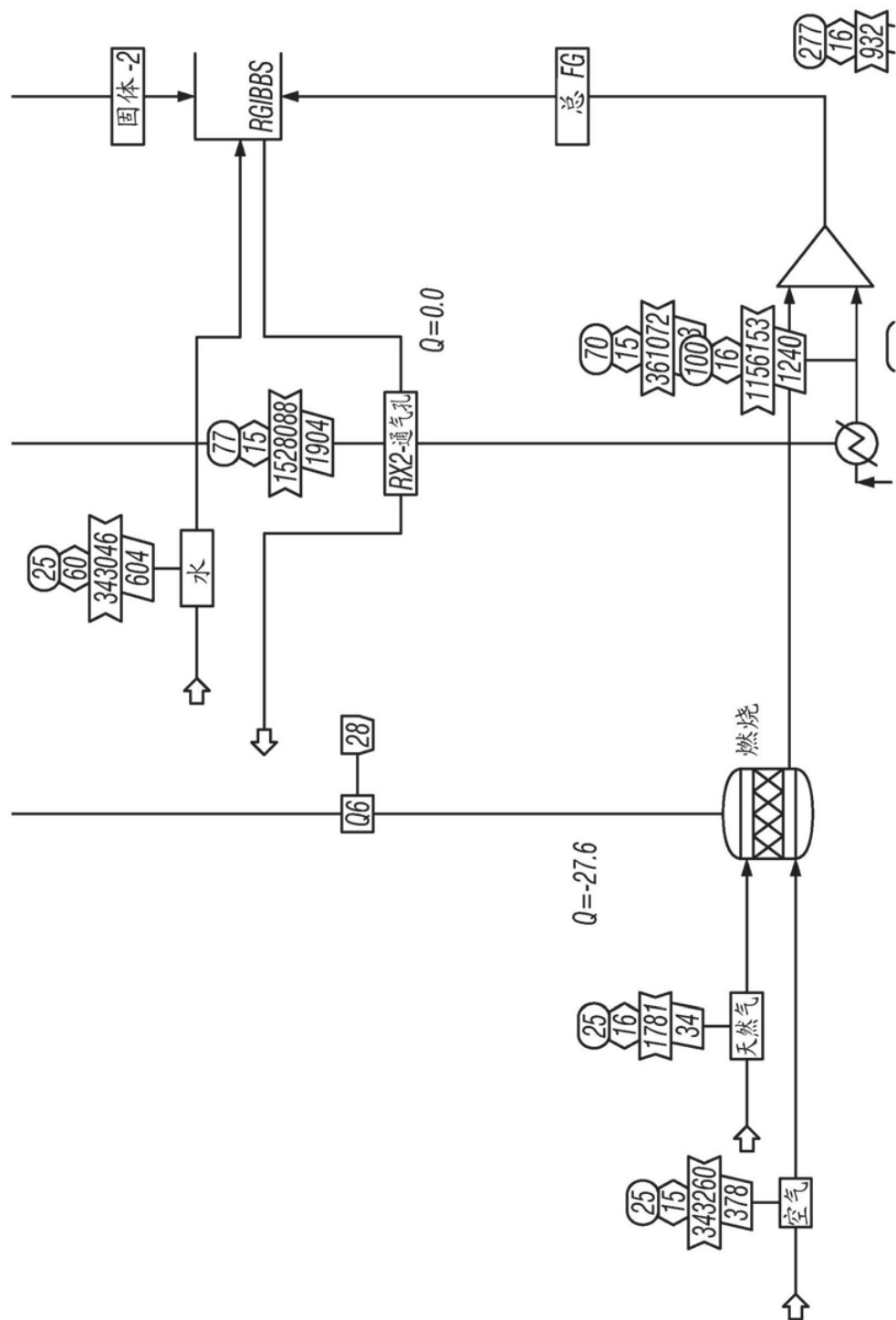


图 39F

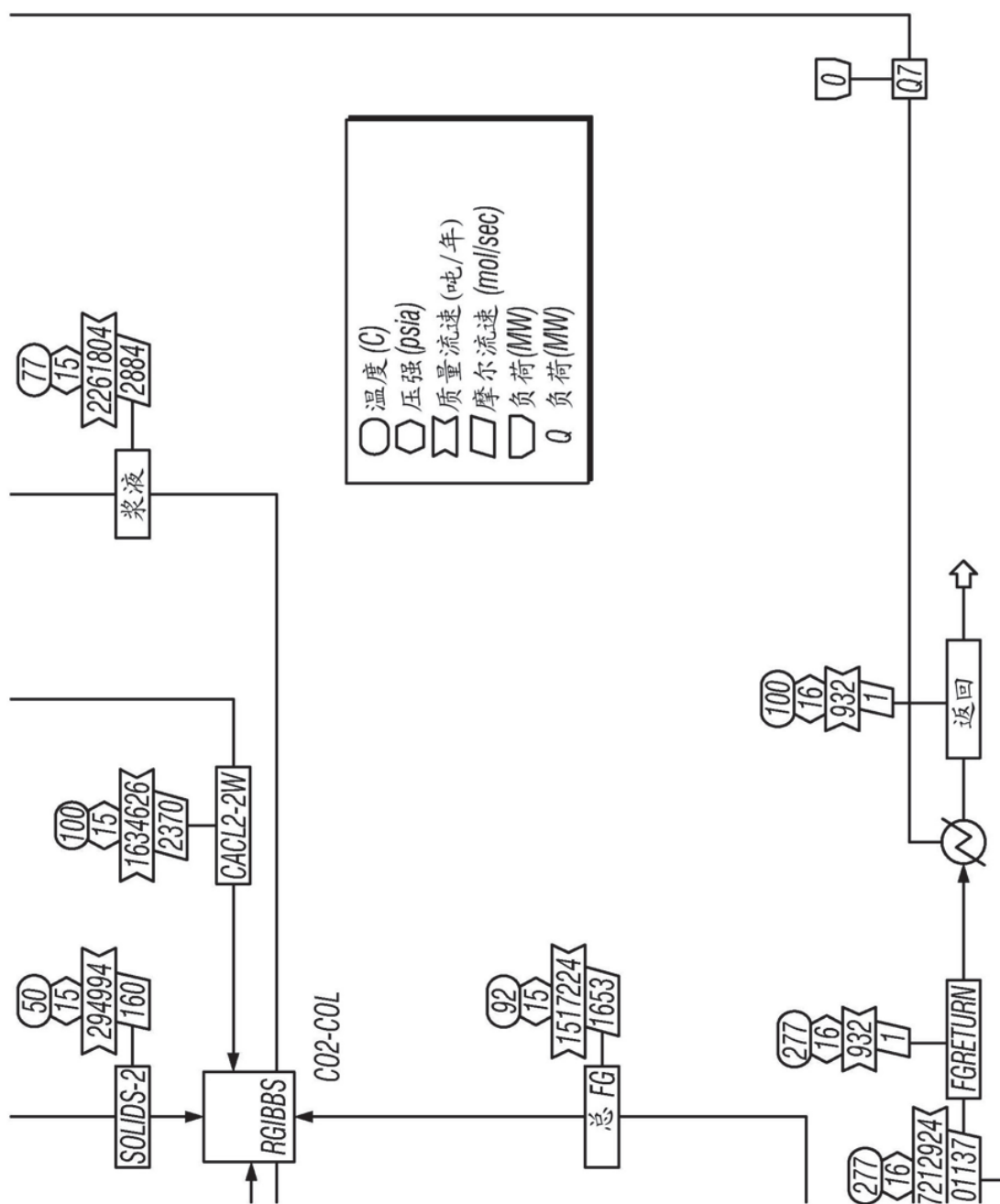


图 39G

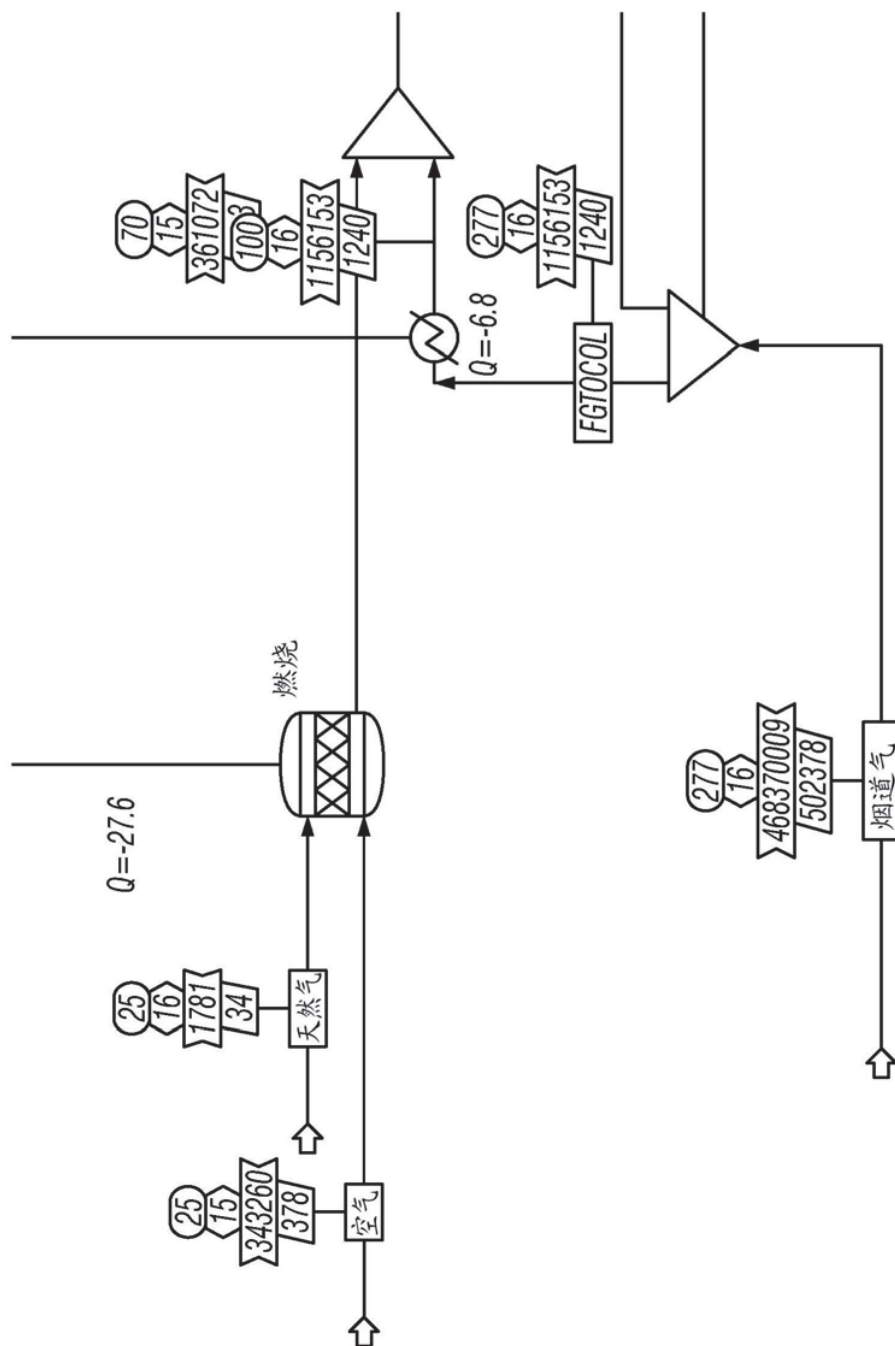


图 39H

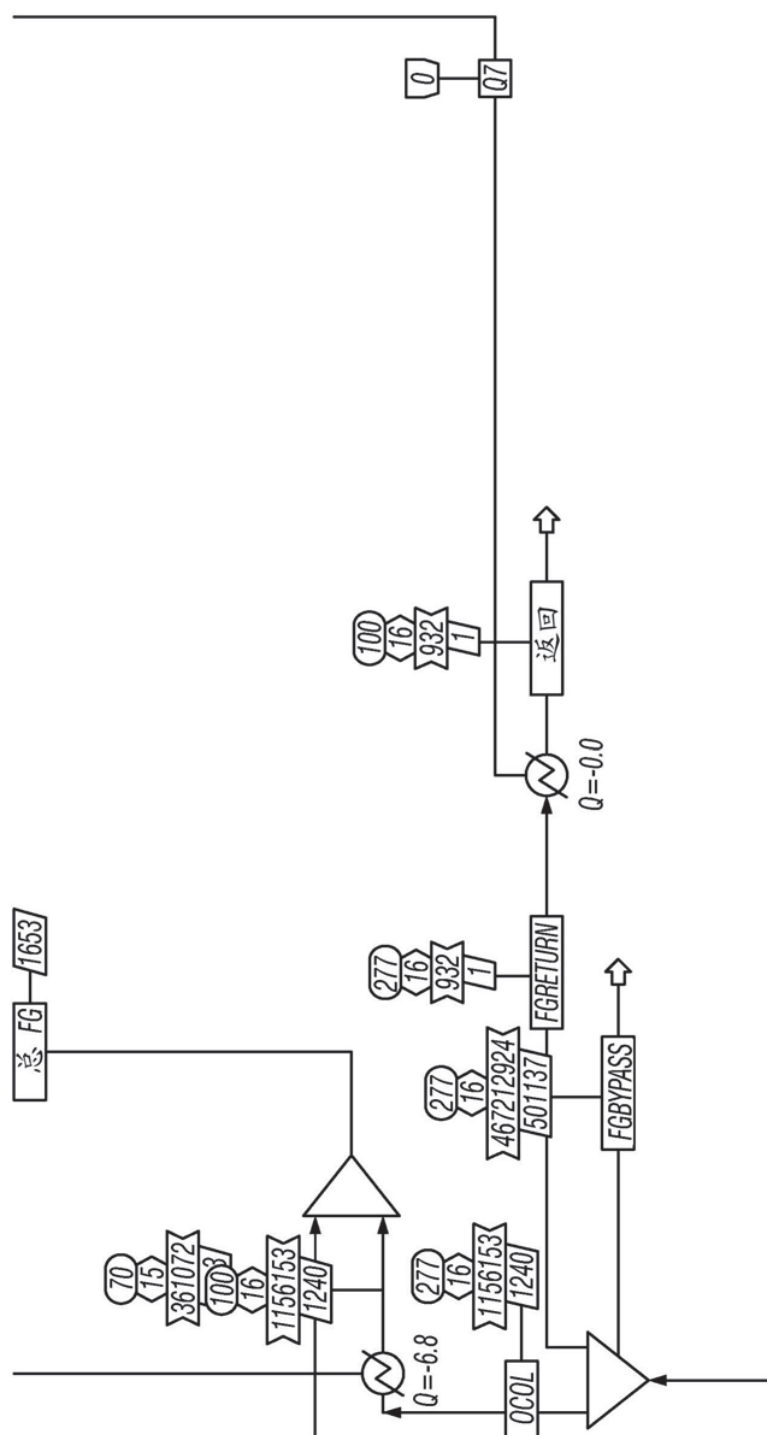


图 39I