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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, MgCI2 is reacted with water under conditions to form Mg(OH)2; and the Mg(OH)2 product is furthe reacted with CaCI2 and carbon dioxide to form MgCI2, CaCO3, and water.

DESCRIPTION

CARBON DIOXIDE SEQUESTRATION INVOLVING TWO-SALT-BASED THERMOLYTIC PROCESSES

BACKGROUND OF THE INVENTION

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 minerals are converted into Group 2 chloride salts and SiO_2, 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 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 CO_2 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 some debate regarding the magnitude of the effect, all would agree there is a benefit to removing CO_2 (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 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 CO_2) 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 $MgCl_2$ 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 $CaCO_3$.

In certain embodiments, the $MgCl_2$ of step (a) is a $MgCl_2$ hydrate (*e.g.*, $MgCl_2{\cdot}6(H_2O)$). In some embodiments, the $MgCl_2$ of step (a) is greater than 90% by weight $MgCl_2{\cdot}6(H_2O)$. 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 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 Mg(OH)Cl. In certain embodiments step (a) occurs in one, two or three reactors.

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 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 $Mg(OH)_2$ product of step (b) can be a solid and separating the step (b) products can comprise separating some or all of the solid $Mg(OH)_2$ from the water and $MgCl_2$ solution. Thus, in some embodiments, the $MgCl_2$ product of step (b) is aqeous $MgCl_2$.

In yet a further embodiment step (b) comprises reacting some or all of the Mg(OH)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 $Mg(OH)_2$ and a second step (b) product comprising $MgCl_2$, wherein the quantity of water is sufficient to provide a molar ratio of water to 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.

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.

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).

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 ($CaMg[Si_2O_6]$), tremolite $Ca_2Mg_5\{[OH]Si_4O_{11}\}_2$ or $CaSiO_3$. In some embodiments, the calcium silicate further comprises iron (*e.g.*, fayalite ($Fe_2[SiO_4]$)) and or manganese silicates.

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 (b) comprise a temperature from about 140 °C to about 240 °C.

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, H_2SO_4 or HNO_3;

(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 $MgCl_2$. In some embodiments, the first cation-based chloride salt or hydrate thereof of step (a) is a hydrated form of $MgCl_2$. In some embodiments, the first cation-based chloride salt or hydrate thereof of step (a) is $MgCl_2 \cdot 6H_2O$. 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 $MgCl_2 \cdot 6H_2O$.

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 ($Mg_2[SiO_4]$). In some embodiments, the Group 2 silicate mineral of step (d) comprises serpentine ($Mg_6[OH]_8[Si_4O_{10}]$). In some embodiments, the Group 2 silicate mineral of step (d) comprises sepiolite ($Mg_4[(OH)_2Si_6O_{15}] \cdot 6H_2O$), enstatite ($Mg_2[Si_2O_6]$), diopside ($CaMg[Si_2O_6]$), and/or tremolite $Ca_2Mg_5\{[OH]Si_4O_{11}\}_2$. In some embodiments, the Group 2 silicate further comprises iron and or manganese silicates. In some embodiments, the iron silicate is fayalite ($Fe_2[SiO_4]$).

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 Mg(OH)Cl of step (a)(i) is greater than 90% by weight Mg(OH)Cl. In some embodiments, the magnesium chloride salt is greater than 90% by weight $MgCl_2 \cdot 6(H_2O)$.

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 CO_2 as Group 2 carbonates according to some embodiments of the present invention.

FIG. 2 is block diagram of a system in which Mg^{2+} functions as a catalyst for the sequestration of CO_2 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 CO_2 as limestone (composed largely of the mineral calcite, $CaCO_3$). The term "road salt" in this figure refers to a Group II chloride, such as $CaCl_2$ and/or $MgCl_2$, either or both of which are optionally hydrated. In embodiments comprising $MgCl_2$, 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 $CaCl_2$, 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.*, $CaCl_2$, and sand (SiO_2).

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 CO_2 as $CaCO_3$. The term "road salt" in this figure refers to a Group II chloride, such as $CaCl_2$ and/or $MgCl_2$, 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.*, $MgCl_2 \cdot 6H_2O$, 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 $CaCl_2$, 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 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 $Mg(OH)_2$. Typically, when $Mg(OH)Cl$ dissolves in water it forms $Mg(OH)_2$ (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 $Mg(OH)_2$. One or more of the aforementioned compounds then reacts with a $CaCl_2/H_2O$ 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:

1st Chamber: $MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O$ 100 °C

2nd Chamber: $MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$ 125 °C

3rd Chamber: $MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O$ 160 °C

(HCl vapor present)

4th Chamber: $MgCl_2 \cdot H_2O \rightarrow Mg(OH)Cl + HCl$ 130 °C

HCl recirculates to the 3rd chamber.

Chamber	**Reaction**	**Model Temp.**	**Preferred Temp. Range**	**Notes**
1st	$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O$	100°C	90°C-120°C	
2nd	$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	125°C	160°C-185°C	
3rd	$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O$	160°C	190°C- 230°C	*

4th	$MgCl_2 \cdot H_2O \rightarrow Mg(OH)Cl + HCl$	130°C	230°C- 260°C	**

* 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 $MgCl_2 \cdot 6H_2O$ results in the formation of Mg(OH)Cl instead of MgO. The Mg(OH)Cl then reacts with H_2O to form $MgCl_2$ and $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ 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:

1st Chamber:	$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O$	100 °C
2nd Chamber:	$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	125 °C
3rd Chamber:	$MgCl_2 \cdot 2H_2O \rightarrow Mg(OH)Cl + HCl + H_2O$	130 °C
3rd Chamber:	$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O$	130 °C

Chamber	Reaction	Model Temp.	Preferred Temp. Range	Notes
1st	$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O$	100°C	90°C-120°C	
2nd	$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$	125°C	160°C-185°C	
3rd	$MgCl_2 \cdot 2H_2O \rightarrow Mg(OH)Cl + HCl + H_2O$	130°C	190°C- 230°C	*
	$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O$			

* 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 Mg(OH)Cl from the $MgCl_2 \cdot 6H_2O$ rather than MgO. The Mg(OH)Cl then reacts with H_2O to form $MgCl_2$ and $Mg(OH)_2$, which reacts with a saturated $CaCl_2/H_2O$ 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 $MgCl_2 \cdot 6H_2O$ to form MgO. The MgO then reacts with H_2O to form $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ 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 termperature range. The preferred range in some emobodiments, is 450 °C – 500 °C. Thus the decomposition goes completely to MgO. The main reaction occurring in this chamber can be represented as follows:

$$MgCl_2 \cdot 6H_2O \rightarrow MgO + 5H_2O + 2HCl \qquad 450\ ^\circ C$$

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 $MgCl_2 \cdot 6H_2O$ is decomposed into an intermediate compound, Mg(OH)Cl at a lower temperature of 250 °C in one chamber. The Mg(OH)Cl is then dissolved in water to form $MgCl_2$ and $Mg(OH)_2$, 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:

$$MgCl_2 \cdot 6H_2O \rightarrow Mg(OH)Cl + HCl + 5H_2O \qquad 250\ ^\circ C$$

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 $MgCl_2 \cdot 6H_2O$. 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.

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 $Mg(OH)_2$ of Example 8.

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

FIG. 14 shows the effect of temperature and pressure on the decomposition of $MgCl_2{\cdot}(H_2O)$.

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

FIG. 16 is a process flow diagram of a variant of the process, whereby only magnesium compounds are used. In this embodiment the Ca^{2+} – 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 making the resulting mineralized carbonate $MgCa(CO_3)_2$ or dolomite.

FIG. 18 – $CaSiO_3$-Mg(OH)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 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 $MgCl_2{\cdot}6H_2O$ 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 $CaCl_2/H_2O$ 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 chloride hexahydrate is dehydrated to magnesium chloride dihydrate $MgCl_2{\cdot}2H_2O$ 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 Mg(OH)Cl. The main reactions occurring in this chamber can be represented as follows:

Reaction	**ΔH** kJ/mole**	**Reaction Temp. Range**
$MgCl_2{\cdot}6H_2O \rightarrow Mg(OH)Cl + 5H_2O + HCl$	433	230 °C – 260 °C
$2HCl(g) + CaSiO_3 \rightarrow CaCl_2(aq) + H_2O + SiO_2\downarrow$	–259	90 °C – 150 °C
$2Mg(OH)Cl + CO_2 + CaCl_2 \rightarrow 2MgCl_2 + CaCO_3\downarrow + H_2O$	–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 – $CaSiO_3$-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 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 indicate that it is efficient to use heat from the HCl reacting with $CaSiO_3$ and heat from flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $MgCl_2{\cdot}6H_2O$ to form MgO. The MgO then reacts with H_2O to form $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ 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 chloride hexahydrate is dehydrated to magnesium chloride dihydrate $MgCl_2{\cdot}2H_2O$ in the first chamber using heat from the HCl and $CaSiO_3$ 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**
$MgCl_2{\cdot}6H_2O \rightarrow MgO + 5H_2O + 2HCl$	560	450 °C – 500 °C
$2HCl(g) + CaSiO_3 \rightarrow CaCl_2(aq) + H_2O + SiO_2\downarrow$	–264	90 °C – 150 °C
$MgO + CO_2 + CaCl_2(aq) \rightarrow MgCl_2(aq) + CaCO_3\downarrow$	–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 – $MgSiO_3$-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 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 $MgCl_2{\cdot}2H_2O$ 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 $MgCl_2{\cdot}2H_2O$ 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**
$MgCl_2{\cdot}2H_2O \rightarrow Mg(OH)Cl + H_2O(g) + HCl(g)$	139.8	230 °C – 260°C
$2HCl(g) + MgSiO_3 \rightarrow MgCl_2 + H_2O + SiO_2\downarrow$	−282.8	90 °C – 150 °C
$2Mg(OH)Cl + CO_2 \rightarrow MgCl_2 + MgCO_3\downarrow + H_2O$	−193.1	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 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 $MgCl_2{\cdot}2H_2O$ 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 $MgCl_2{\cdot}2H_2O$ 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
$MgCl_2{\cdot}2H_2O \rightarrow MgO + H_2O(g) + 2HCl(g)$	232.9	450 °C – 500°C
$2HCl(g) + MgSiO_3 \rightarrow MgCl_2(aq) + H_2O(g) + SiO_2\downarrow$	−293.5	90 °C – 150 °C
$MgO + CO_2 \rightarrow MgCO_3\downarrow$	−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 $MgCa(SiO_3)_2$, CO_2 and water, to form SiO_2 and dolomite $MgCa(CO_3)_2$. Results from this simulation indicate that it is efficient to use heat from the HCl reacting with $MgCa(SiO_3)_2$ and heat from the flue gas emitted by a natural gas or coal fired power plant to carry out the decomposition of $MgCl_2{\cdot}6H_2O$ 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 $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $MgCa(CO_3)_2$ 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 $MgCl_2{\cdot}2H_2O$ 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
$MgCl_2{\cdot}6H_2O \rightarrow Mg(OH)Cl + 5H_2O(g) + HCl(g)$	433	230 °C – 260 °C
$2HCl(g) + MgCa(SiO_3)_2 \rightarrow CaCl_2(aq) + MgSiO_3\downarrow + SiO_2\downarrow + H_2O$	−235	90 °C – 150 °C
$2HCl(g) + MgSiO_3 \rightarrow MgCl_2(aq) + SiO_2\downarrow + H_2O$	−282.8	90 °C – 150 °C
$4Mg(OH)Cl + 2CO_2 + CaCl_2(aq) \rightarrow MgCa(CO_3)_2\downarrow + 3MgCl_2(aq) + 2H_2O$	−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 CO_2 from flue gas using inexpensive raw materials, diopside $MgCa(SiO_3)_2$, CO_2 and water, to form SiO_2 and dolomite $MgCa(CO_3)_2$. Results from this simulation indicate that it is efficient to use heat from the HCl reacting with $MgCa(SiO_3)_2$ 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 $MgCl_2{\cdot}6H_2O$ to form MgO. The MgO then reacts with H_2O to form $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $MgCa(CO_3)_2$ 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 $MgCl_2{\cdot}2H_2O$ in the first chamber using heat from the HCl and $CaSiO_3$ 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**
$MgCl_2{\cdot}6H_2O \rightarrow MgO + 5H_2O + 2HCl$	560	450 °C – 500°C
$2HCl(g) + MgCa(SiO_3)_2 \rightarrow CaCl_2(g) + MgSiO_3\downarrow + SiO_2\downarrow + H_2O$	−240	90 °C – 150 °C
$2HCl(aq) + MgSiO_3 \rightarrow MgCl_2(aq) + SiO_2\downarrow + H_2O$	−288	90 °C – 150 °C
$2MgO + 2CO_2 + CaCl_2(aq) \rightarrow MgCa(CO_3)_2\downarrow + MgCl_2(aq)$	−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 CO_2 captured for varying CO_2 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 $CaSiO_3$-$Mg(OH)Cl$ and $CaSiO_3$-MgO processes.

FIG. 25 illustrates the percent CO_2 captured for varying CO_2 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 $MgSiO_3$-$Mg(OH)Cl$ and $MgSiO_3$-MgO processes.

FIG. 26 illustrates the percent CO_2 captured for varying CO_2 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.*, Ca^{2+} and Mg^{2+}, are used for decomposition and carbonation.

FIGS. 28-29 show graphs of the mass percentages of heated samples of $MgCl_2 \cdot 6H_2O$. 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 was 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 – $MgCl_2 \cdot 6H_2O$ Decomposition at 500°C after One Hour. This graph shows the normalized final and initial weights of four test runs of $MgCl_2 \cdot 6H_2O$ 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 Mg(OH)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 Mg(OH)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 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 natural gas as an external source of the remaining heat which

is 13% 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. 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 CO_2 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 $MgCl_2{\cdot}6H_2O$ to M(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 $CaSiO_3$-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 CO_2 from flue gas using inexpensive raw materials, $CaSiO_3$, CO_2 and water, to form SiO_2 and $CaCO_3$. Heat is used to carry out the decomposition of $MgCl_2{\cdot}6H_2O$ to form Mg(OH)Cl. The Mg(OH)Cl then reacts with H_2O to form $MgCl_2$ and $Mg(OH)_2$. The quantity of H_2O is regulated to favor formation of solid $Mg(OH)_2$ and aqueous $MgCl_2$ (which is recycled to the first reactor to begin the process again). The $Mg(OH)_2$ then reacts with a saturated $CaCl_2/H_2O$ 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.

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 CO_2 from flue gas using inexpensive raw materials, $CaSiO_3$, CO_2 and water, to form SiO_2 and $CaCO_3$. Heat is used to carry out the decomposition of $MgCl_2{\cdot}6H_2O$ to form Mg(OH)Cl. The Mg(OH)Cl then reacts with H_2O to form $MgCl_2$ and $Mg(OH)_2$. The quantity of H_2O is regulated to favor formation of solid $Mg(OH)_2$ and aqueous $MgCl_2$ (which is recycled to the first reactor to begin the process again). The $Mg(OH)_2$ then reacts with a saturated $CaCl_2/H_2O$ 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. 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 CO_2 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 CO_2 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 CO_2 from a given source, such as a power plant.

Another additional benefit of certain embodiments of the present invention that distinguishes them from other CO_2-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 CO_2 and incidental pollutants of concern.

I. Definitions

As used herein, the terms "carbonates" or "carbonate products" are generally defined as mineral components containing the carbonate group, $[CO_3]^{2-}$. 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, $[HCO_3]^{1-}$. 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 CO_2 sequestered by certain embodiments of the present invention per energy consumed (represented by the equation "$\partial CO_2/\partial E$"), appropriate units for this value are kWh/ton CO_2. CO_2 sequestration is denominated in terms of percent of total plant CO_2; 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 $MgCl_2 \cdot 6H_2O$.

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 ($Ca(HCO_3)_2$) 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.

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.

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.

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 $XY(Si,Al)_2O_6$, where X represents calcium, sodium, iron (II) and 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 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 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.

$$(\mathrm{Ca/Mg})\mathrm{Cl_2} + 2\ \mathrm{H_2O} \rightarrow (\mathrm{Ca/Mg})(\mathrm{OH})_2 + 2\ \mathrm{HCl} \qquad (1)$$

The water used in this reaction may be in the form of liquid, steam, a crystalline hydrate, *e.g.*, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, or it may be supercritical. In some embodiments, the reaction uses $MgCl_2$ to form $Mg(OH)_2$ and/or $Mg(OH)Cl$ (see, *e.g.*, FIG. 2). In some embodiments, the reaction uses $CaCl_2$ to form $Ca(OH)_2$. 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.

$$(Ca/Mg)(OH)_2 + CO_2 \rightarrow (Ca/Mg)CO_3 + H_2O \qquad (2)$$

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 CO_2 and/or other pollutants have been removed, is released to the air.

Group 2 silicates (*e.g.*, $CaSiO_3$, $MgSiO_3$, $MgO \cdot FeO \cdot SiO_2$, 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 ($CaCl_2$ and/or $MgCl_2$), water and sand (SiO_2). The reaction can be represented by equation 3.

$$2\,HCl + (Ca/Mg)SiO_3 \rightarrow (Ca/Mg)Cl_2 + H_2O + SiO_2 \qquad (3)$$

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:

$$CO_2 + (Ca/Mg)SiO_3 \rightarrow (Ca/Mg)CO_3 + SiO_2 \qquad (4)$$

In another embodiment, the resulting $Mg_xCa_{(1-x)}CO_3$ 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.

$$\begin{gathered} MgCl_2{\cdot}x(H_2O) + yH_2O \rightarrow \\ z'[Mg(OH)_2] + z''[MgO] + z'''[MgCl(OH)] + (2z' + 2z'' + z''')[HCl] \qquad (5) \end{gathered}$$

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 of 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 $CaCl_2$ (*e.g.*, rock salt). The carbon dioxide reacts with the magnesium salt product and $CaCl_2$ in reactor **200** according to the reaction represented by equation 6.

$$CO_2 + CaCl_2 + z'[Mg(OH)_2] + z''[MgO] + z'''[MgCl(OH)] \rightarrow$$
$$(z' + z'' + z''')MgCl_2 + (z' + \tfrac{1}{2}z''')H_2O + CaCO_3 \qquad (6)$$

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 CO_2 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 $MgCl_2$ product, optionally hydrated, is returned to reactor **100**. In some embodiments, the $MgCl_2$ product is subjected to one or more isolation, purification and/or hydration steps before being returned to reactor **100**.

Calcium silicate (*e.g.*, $3CaO{\cdot}SiO_2$, Ca_3SiO_5; $2CaO{\cdot}SiO_2$, Ca_2SiO_4; $3CaO{\cdot}2SiO_2$, $Ca_3Si_2O_7$ and $CaO{\cdot}SiO_2$, $CaSiO_3$ 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 $CaSiO_3$ (*e.g.*, wollastonite, which may itself, in some embodiments, contain small amounts of iron, magnesium and/or manganese substituting for iron). The $CaSiO_3$ 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 $CaCl_2$, water and sand (SiO_2). The reaction can be represented by equation 7.

$$2\,HCl + (Ca/Mg)SiO_3 \rightarrow (Ca/Mg)Cl_2 + H_2O + SiO_2 \qquad (7)$$

Reaction	**ΔH kJ/mole****	**Reaction Temp. Range**
$2\,HCl(g) + CaSiO_3 \rightarrow CaCl_2 + H_2O + SiO_2$	−254	90 °C – 150 °C
$2\,HCl(g) + MgSiO_3 \rightarrow MgCl_2(aq) + H_2O + SiO_2$	−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:

$$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2 \qquad (8)$$

Reaction	**ΔH kJ/mole****	**ΔG kJ/mole****
$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$	−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:

$$MgCl_2 + 2\ H_2O \rightarrow Mg(OH)_2 + 2\ HCl(g) \qquad \Delta H = 263\text{ kJ/mole}^{**} \qquad (9)$$

$$CaCl_2 + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ HCl(g) \qquad \Delta H = 284\text{ kJ/mole}^{**} \qquad (10)$$

**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 of more of the following steps:

$$CaCl_2 + (x + y + z)\ H_2O \rightarrow Ca^{2+}\cdot xH_2O + Cl^-\cdot yH_2O + Cl^-\cdot zH_2O \qquad (11)$$

$$\begin{gathered} Ca^{+2}\cdot xH_2O + Cl^-\cdot yH_2O + Cl^-\cdot zH_2O \rightarrow \\ [Ca^{2+}\cdot(x-1)(H_2O)OH^-]^+ + Cl^-\cdot(yH_2O) + Cl^-\cdot(z-1)H_2O + H_3O^+ \end{gathered} \qquad (12)$$

$$[Ca^{2+}\cdot(x-1)(H_2O)OH^-]^+ + Cl^-\cdot(yH_2O) + Cl^-\cdot(z-1)H_2O + H_3O^+ \rightarrow$$
$$[Ca^{2+}\cdot(x-1)(H_2O)OH^-]^+ + Cl^-\cdot(yH_2O)^- + zH_2O + HCl(g)\uparrow \quad (13)$$

$$[Ca^{2+}\cdot(x-1)(H_2O)OH^-]^+ + Cl^-\cdot(yH_2O) \rightarrow$$
$$[Ca^{2+}\cdot(x-2)(H_2O)\ (OH^-)_2] + Cl^-\cdot(y-1)H_2O + H_3O^+ \quad (14)$$

$$[Ca^{2+}\cdot(x-2)(H_2O)\ (OH^-)_2] + Cl^-\cdot(y-1)H_2O + H_3O^+ \rightarrow$$
$$Ca(OH)_2\downarrow + (x-2)H_2O + yH_2O + HCl\uparrow \quad (15)$$

The reaction enthalpy (ΔH) for $CaCl_2 + 2\ H_2O \rightarrow Ca(OH)_2 + 2\ HCl(g)$ is 284 kJ/mole at 100 °C. In some variants, the salt $MgCl_2\cdot 6H_2O$, 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:

$$MgCl_2\cdot 6H_2O \rightarrow MgCl_2\cdot 4H_2O + 2\ H_2O \quad (16)$$

$$MgCl_2\cdot 4H_2O \rightarrow MgCl_2\cdot 2H_2O + 2\ H_2O \quad (17)$$

From 135-180 °C:

$$MgCl_2\cdot 4H_2O \rightarrow Mg(OH)Cl + HCl + 3\ H_2O \quad (18)$$

$$MgCl_2\cdot 2H_2O \rightarrow MgCl_2\cdot H_2O + H_2O \quad (19)$$

From 185-230 °C:

$$MgCl_2\cdot 2H_2O \rightarrow Mg(OH)Cl + HCl + H_2O \quad (20)$$

From >230 °C:

$$MgCl_2\cdot H_2O \rightarrow MgCl_2 + H_2O \quad (21)$$

$$MgCl_2\cdot H_2O \rightarrow Mg(OH)Cl + HCl \quad (22)$$

$$Mg(OH)Cl \rightarrow MgO + HCl \quad (23)$$

Reaction	**Referenced Temp. Range**	**ΔH kJ/mole****	**Temp. Reaction**
$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2\ H_2O(g)$	95 °C – 110 °C	115.7	100°C
$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2\ H_2O(g)$	95 °C – 110 °C	134.4	100°C
$MgCl_2 \cdot 4H_2O \rightarrow Mg(OH)Cl + HCl(g) + 3\ H_2O(g)$	135 °C – 180 °C	275	160°C
$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O(g)$	135 °C – 180 °C	70.1	160°C
$MgCl_2 \cdot 2H_2O \rightarrow Mg(OH)Cl + HCl(g) + H_2O(g)$	185 °C – 230 °C	141	210°C
$MgCl_2 \cdot H_2O \rightarrow MgCl_2 + H_2O(g)$	>230 °C	76.6	240°C
$MgCl_2 \cdot H_2O \rightarrow Mg(OH)Cl + HCl(g)$	>230 °C	70.9	240°C
$Mg(OH)Cl \rightarrow MgO + HCl(g)$	>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 CO_2 from flue gas using an inexpensive raw material, $CaCl_2$, to form $CaCO_3$. 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 $MgCl_2.6H_2O$ 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 $MgCl_2$ (via Mg(OH)Cl) by adjusting the proportion of $MgCl_2$ 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 $MgCl_2 \cdot 6(H_2O)$ hydrates. Specifically, the amount of water in a Mg(OH)Cl solution is maintained at a water to $MgCl_2$ molar ratio of greater than or equal to 6, such as a ratio of 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 $MgCl_2 \cdot 6H_2O$ and $Mg(OH)_2$ Mg(OH)Cl is reacted with an aqueous $MgCl_2$ solution, such as that from the bubble column. That reaction would be:

$$CaCl_2(aq) + CO_2 + Mg(OH)_2 \Rightarrow MgCl_2(aq) + CaCO_3 \downarrow + H_2O$$

$$MgCl_2(aq) \sim MgCl_2 \cdot 13\text{-}16H_2O(liquid)$$

Boiling the mixture $MgCl_2 \cdot 13\text{-}16H_2O(liquid) + \Delta H \Rightarrow MgCl_2 \cdot 6H_2O(solid) + 7\text{-}9H_2O(gas)\uparrow$ would require significant energy usage. Thus, a solution more dilute than $MgCl_2 \cdot 6H_2O$ shall cause the disproportionation of Mg(OH)Cl, a solution of $MgCl_2.xH_2O(liquid)$ where $x \geq 12$ should also be able to cause the disproportionation of Mg(OH)Cl. The equation is written as follows:

$$Mg(OH)Cl + \tfrac{1}{2} MgCl_2 \cdot 13\text{-}16H_2O(liquid) \Rightarrow \tfrac{1}{2} Mg(OH)_2 + MgCl_2 \cdot 6.5\text{-}8H_2O$$

Such as: $Mg(OH)Cl + \tfrac{1}{2} MgCl_2 \cdot 12H_2O(liquid) \Rightarrow \tfrac{1}{2} Mg(OH)_2 + MgCl_2 \cdot 6H_2O$

The $MgCl_2(aq)$ is being reconstituted to half of the original $MgCl_2 \cdot 6H_2O$ by water removal and the remaining half of the $MgCl_2 \cdot 6H_2O$ forms from the disproportionation of Mg(OH)Cl by addition of water.

An example of a system that utilizes $Mg(OH)_2$ 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, 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 MgC12 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 ($MgCl_2.6H_2O$ almost) and stream SOLIDS-2, which is the $Mg(OH)_2$ 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

CO_2. 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 CO_2 based on one or both of the following reactions:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (24)$$

$$\Delta H = -117.92 \text{ kJ/mol}^{**}$$
$$\Delta G = -79.91 \text{ kJ/mol}^{**}$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \qquad (25)$$

$$\Delta H = -58.85 \text{ kJ/mol}^{**}$$
$$\Delta G = -16.57 \text{ kJ/mol}^{**}$$

** 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 discontinous 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 CO_2 from flue gas using an inexpensive raw material, $Ca(CO)_2$ derived from $CaCl_2$, to form $CaCO_3$.

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:

$$CaCl_2 + MgCO_3 +\!\!\rightarrow MgCl_2 + CaCO_3 \qquad (25a)$$

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 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 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, 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 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 ($CaMgSi_2O_6$).

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

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \tag{26}$$

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 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, magnesium, and manganese substituting for calcium.

In some embodiments, compositions comprising olivine and/or serpentine may be used. CO_2 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 $(Mg,Fe)_2SiO_4$. 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 magna 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 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.

VII. Generation of Group 2 Chlorides from Group 2 Silicates

Group 2 silicates, *e.g.*, $CaSiO_3$, $MgSiO_3$, 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 ($CaCl_2$ and/or $MgCl_2$), water and sand. In some embodiments the HCl produced in equation 1 is used to regenerate the $MgCl_2$ and/or $CaCl_2$ 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. SiO_2 was observed to precipitate out and $MgCl_2$ and $CaCl_2$ were collected.

Table 1. Calcium/Magnesium Minerals.

Mineral	**Formula (std. notation)**	**Formula (oxide notation)**	**Ratio Group 2:SiO_2**	**Ratio Group 2: total**
Olivine	$(Mg,Fe)_2[SiO_4]$	$(MgO,FeO)_2 \cdot SiO_2$	1:1	1:2
Serpentine	$Mg_6[OH]_8[Si_4O_{10}]$	$6MgO \cdot 4SiO_2 \cdot 4H_2O$	3:2	undefined
Sepiolite	$Mg_4[(OH)_2Si_6O_{15}]6H_2O$	$3MgO \cdot Mg(OH)_2 \cdot 6SiO_2 \cdot 6H_2O$	2:3	undefined
Enstatite	$Mg_2[Si_2O_6]$	$2MgO \cdot 2SiO_2$	1:1	undefined
Diopside	$CaMg[Si_2O_6]$	$CaO \cdot MgO \cdot 2SiO_2$	1:1	undefined
Tremolite	$Ca_2Mg_5\{[OH]Si_4O_{11}\}_2$	$2CaO \cdot 5MgO \cdot 8SiO_2H_2O$	7:8	undefined
Wollastonite	$CaSiO_3$	$CaO \cdot SiO_2$	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 (thermogravinometric 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

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.

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.

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.

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:

$2NaI + H_2O \rightarrow Na_2O + 2HI$ and/or $Na_2O + H_2O \rightarrow 2NaOH$

$MgCl_2{\cdot}6H_2O \rightarrow MgO + 5H_2O + 2HCl$ and/or $MgO + H_2O \rightarrow Mg(OH)_2$

Examples of a Decarbonation:

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ and/or $Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$

$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$ and/or $Mg(OH)_2 + 2CO_2 \rightarrow Mg(HCO_3)_2$

Examples of a Carbonate exchange with a Salt-2:

$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3\downarrow + 2NaCl$

$Na_2CO_3 + 2AgNO_3 \rightarrow Ag_2CO_3\downarrow + 2NaNO_3$

$Ca(OH)_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaOH$*

* 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, 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, $CdCO_3$, $Al_2(CO_3)_3$, Tl_2CO_3, $PbCO_3$, and $La_2(CO_3)_3$. 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, 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 $MgCl_2{\cdot}6H_2O$. Table E below, summarizes these salts and the percent penalty reduction through their use relative to $MgCl_2.6H_2O$.

Table E: Section Lower Energy Alternative Salts

Compound	kw-hr/tonne	% reduction
$MgCl_2.6H2O$	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%
$FeCl_2.4H_2O$	3860	17%
$FeI_2.4H_2O$	3055	47%
$CoCl_2.6H_2O$	3860	17%
$CoI_2.6H_2O$	4123	9%
$CoSO_4.4H_2O$	3351	34%
$ZnF_2.2H_2O$	3285	37%
$ZnBr_2.4H_2O$	4418	2%
$ZnI_2.4H_2O$	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
$MgCl_2\cdot 6H_2O$	4500	
$MnCl_2\cdot 4H_2O$	5043	only Mn^{+2} forms a stable carbonate
$NaI\cdot 2H_2O$	1023	too rare
$CoI_2\cdot 6H_2O$	4123	too rare
$FeCl_2\cdot 4H_2O$	3860	May oxidize to ferric oxide, this will not form a stable carbonate
LiBr	3006	too rare
$Mg(NO_3)_2\cdot 4H_2O$	1606	leaves Nox
$CoSO_4\cdot 4H_2O$	3351	somewhat rare leaves SO_3
$CdCl_2\cdot 2.5H_2O$	not aval.	toxic byproducts
$Ca(NO_3)_2\cdot 4H_2O$	2331	leaves NO_2

Compound	References
$MgCl_2\cdot 6H_2O$	
$MnCl_2\cdot 4H_2O$	http://avogadro.chem.iastate.edu/MSDS/MnCl2.htm
$NaI_2\cdot H_2O$	http://www.chemicalbook.com/ProductMSDSDetailCB6170714_EN.htm
$CoI_2\cdot 6H_2O$	http://www.espimetals.com/index.php/msds/527-cobalt-iodide
$FeCl_2\cdot 4H_2O$	
LiBr	http://www.chemcas.com/material/cas/archive/7550-35-8_v1.asp
$Mg(NO_3)_2\cdot 4H_2O$	http://avogadro.chem.iastate.edu/MSDS/MgNO3-6H2O.htm

$CoSO_4.4H_2O$	http://www.chemicalbook.com/ProductMSDSDetailCB0323842_EN.htm
$CdCl_2{\cdot}2.5H2O$	http://www.espimetals.com/index.php/msds/460-cadmium-chloride
$Ca(NO_3)_2{\cdot}4H2O$	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: $CaCO_3$). 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. $CaCO_3$ 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, $MgCO_3$, is a white solid that occurs in nature as a mineral. The most common magnesium carbonate forms are the anhydrous salt called magnesite ($MgCO_3$) and the di, tri, and pentahydrates known as barringtonite ($MgCO_3{\cdot}2H_2O$), nesquehonite ($MgCO_3{\cdot}3H_2O$), and lansfordite ($MgCO_3{\cdot}5H_2O$), 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, $CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $Ca(OH)_2$, $Ca(OH)_2$, 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 CO_2 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:

$$Cl_2(g) + 2\ H_2O\ (l) + h\nu\ (363\ \text{nm}) \rightarrow 2\ HCl\ (l) + \tfrac{1}{2}\ O_2\ (g) \qquad (27)$$

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 CO_2 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.

$$Ca/Mg(OH)_2 + Cl_2 \rightarrow \tfrac{1}{2}\ Ca/Mg(OCl)_2 + \tfrac{1}{2}\ Ca/MgCl_2 + H_2O \qquad (28)$$

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

$$Ca/Mg(OCl)_2 \rightarrow Ca/MgCl_2 + O_2 \qquad (29)$$

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

XV. Removal of other Pollutants from Source

In addition to removing CO_2 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 CO_2 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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

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 CO_2 from a flue gas stream utilizing $CaCl_2$ and heat to form $CaCO_3$ product. These results show that it is possible to capture CO_2 from flue gas using inexpensive raw materials, $CaCl_2$ and water, to form $CaCO_3$.

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 $CaCl_2/H_2O$ 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 $MgCl_2$/water solution causing it to break down into a HCl/H_2O vapor stream and a liquid stream of $Mg(OH)_2$. The HCl/H_2O 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:

$$MgCl_2 + 2\ H_2O \rightarrow Mg(OH)_2 + 2HCl \qquad (30)$$

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:

$$Mg(OH)_2 + CaCl_2 + CO_2 \rightarrow CaCO_3\ (s) + MgCl_2 + H_2O \qquad (31)$$

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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

Process Stream Names →	1	2	3	BOTTOMS	$CaCl_2$	$CaCO_3$	FG-IN	H_2O	H_2O-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_2O	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									
$MgCl_2$									
$MgCO_3$									
$Ca(O)Cl_2$									
$CaCl_2O_2$									
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_2O	H_2O-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_2O	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_2O	H_2O-MgOH
$Mg(OH)_2$									
Mg(OH)Cl									
$MgCl_2$									
$MgCO_3$									
$Ca(O)Cl_2$									
$CaCl_2O_2$									
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_2O**	**H_2O-MgOH**
H_2O	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									
$MgCl_2$									
$MgCO_3$									
$Ca(O)Cl_2$									
$CaCl_2O_2$									
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_2O	H_2O-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_2O	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									
$MgCl_2$									
$MgCO_3$									
$Ca(O)Cl_2$									
$CaCl_2O_2$									
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_2O	H_2O-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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

Process Stream Names →	H_2O-IN	HCl-H_2O	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_2O-IN	HCl-H_2O	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_2O	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						
$MgCl_2$						
$MgCO_3$						
$Ca(O)Cl_2$						
$CaCl_2O_2$						
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_2O-IN	HCl-H_2O	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_2O	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_2O-IN**	**HCl-H_2O**	**Mg-$CaCl_2$**	**MgOH-O1**	**RETURN**	**RX3-VENT**
Mg(OH)Cl						
$MgCl_2$						
$MgCO_3$						
$Ca(O)Cl_2$						
$CaCl_2O_2$						
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_2O-IN	HCl-H_2O	Mg-$CaCl_2$	MgOH-O1	RETURN	RX3-VENT
H_2O	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						
$MgCl_2$						
$MgCO_3$						
$Ca(O)Cl_2$						
$CaCl_2O_2$						
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_2O-IN	HCl-H_2O	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_2O	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						
$MgCl_2$						
$MgCO_3$						
$Ca(O)Cl_2$						
$CaCl_2O_2$						
Ca^{2+}					57 PPM	

Process Stream Names →	H_2O-IN	HCl-H_2O	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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

Results from the simulation suggest that it is efficient to heat a $MgCl_2 \cdot 6H_2O$ 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 H_2O to form $MgCl_2$ and $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $CaCO_3$, which is filtered out of the stream. The resulting $MgCl_2 \cdot 6H_2O$ 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 $CaCl_2$. 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.
- 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 CO_2. 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 $MgCl_2 \cdot 6H_2O$ causing it to break down into a HCl/H_2O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H_2O 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:

$$MgCl_2 \cdot 6H_2O + \Delta \rightarrow Mg(OH)Cl + 5\ H_2O\uparrow + HCl\uparrow \qquad (32)$$

$$2\ Mg(OH)Cl(aq) \rightarrow Mg(OH)_2 + MgCl_2 \qquad (33)$$

A $CaCl_2$ solution and a flue gas stream are added to the $Mg(OH)_2$ 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. Chemical reaction(s) occurring in this reactor include the following:

$$Mg(OH)_2 + CaCl_2 + CO_2 \rightarrow CaCO_3 \downarrow(s) + MgCl_2 + H_2O \qquad (34)$$

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_2O	H_2O-1	H_2O-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_2O	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_2O	H_2O-1	H_2O-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_2O	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_2O	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_2O**	**H_2O-1**	**H_2O-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 VFrac	0	0	0	0	1	0	0	0	1
Mass SFrac	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_2O	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_2O	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
$Ca(O)Cl_2$	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	RECYCIE1	RX2-VENT	SLURRY	SOLIDS-1	SOLIDS-2	VAPOR
H_2O	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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

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 $MgCl_2{\cdot}6H_2O$ 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 H_2O to form $MgCl_2$ and $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $CaCO_3$, which is filtered out of the stream. The resulting $MgCl_2.6H_2O$ 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 4862 kwh/tonne CO_2. 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 $MgCl_2.6H_2O$ causing it to break down into a HCl/H_2O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H_2O 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:

$$MgCl_2{\cdot}6H_2O + \Delta \rightarrow Mg(OH)Cl + 5\ H_2O\uparrow + HCl\uparrow \qquad (35)$$

$$2\ Mg(OH)Cl(aq) \rightarrow Mg(OH)_2 + MgCl_2 \qquad (36)$$

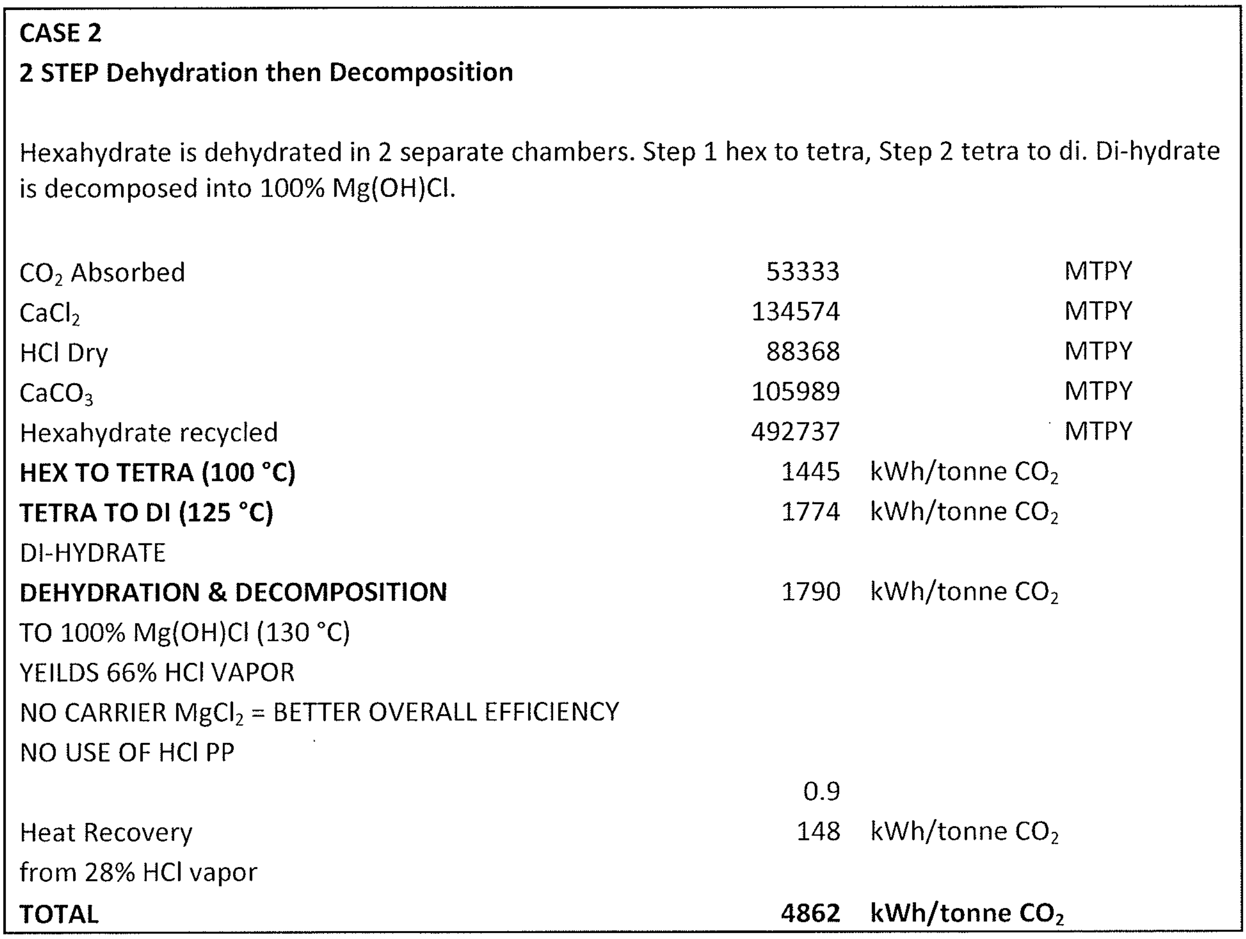
A $CaCl_2$ solution and a flue gas stream are added to the $Mg(OH)_2$ in reactor 2. This reaction forms $CaCO_3$, $MgCl_2$ and water. The $CaCO_3$ precipitates and is removed in a filter or decanter. The remaining $MgCl_2$ and water are recycled to the first reactor. Additional water is added to complete the water balance required by the first reactor. Chemical reaction(s) occurring in this reactor include the following:

$$Mg(OH)_2 + CaCl_2 + CO_2 \rightarrow CaCO_3 \downarrow(s) + MgCl_2 + H_2O \qquad (37)$$

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 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% Mg(OH)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% Mg(OH)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_2O	H_2O-1	H_2O-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_2O	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_2O	H_2O-1	H_2O-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_2O	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
MgCl2*4W	0	1	0	0	0	0	0	0	0	0
MgCl2*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_2O	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_2O	H_2O-1	H_2O-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_2O	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_2O	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_2O	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 CO_2 from Flue Gas Using $CaCl_2$ to Form $CaCO_3$.

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 $MgCl_2 \cdot 6H_2O$ stream to form MgO in a single chamber. The MgO is reacted with H_2O to form $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $CaCO_3$, which is filtered out of the stream. The resulting $MgCl_2 \cdot 6H_2O$ 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 3285 kwh/tonne CO_2. 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 $MgCl_2 \cdot 6H_2O$ causing it to break down into a HCl/H_2O vapor stream and a solid stream of MgO. The HCl/H_2O 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:

$$MgCl_2 \cdot 6H_2O + \Delta \rightarrow MgO + 5\ H_2O\uparrow + 2\ HCl\uparrow \qquad (38)$$

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (39)$$

A $CaCl_2$ solution and a flue gas stream are added to the $Mg(OH)_2$ 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. Chemical reaction(s) occurring in this reactor include the following::

$$Mg(OH)_2 + CaCl_2 + CO_2 \rightarrow CaCO_3 \downarrow(s) + MgCl_2 + H_2O \qquad (40)$$

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 3) are summarized below:

CASE 3

Combined Dehydration/Decomposition to MgO

Hexahydrate is dehydrated and decomposed simultaneously at 450C. Reactor yeilds 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 CO2
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 CO2
from 45% HCl vapor		
TOTAL	3285	kWh/tonne CO2

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

Process Stream Names →	$CaCl_2$	$CaCO_3$	FLUE GAS	H_2O	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_2O	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_2O**	**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_2O	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_2O	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_2O	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_2O	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_2O	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_2O	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 CO_2 from Flue Gas Using $CaCl_2$ to form $CaCO_3$.

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 $MgCl_2{\cdot}6H_2O$ stream to form Mg(OH)Cl in a single chamber. The Mg(OH)Cl is reacted with H_2O to form $MgCl_2$ and $Mg(OH)_2$, which then reacts with a saturated $CaCl_2/H_2O$ solution and CO_2 from the flue gas to form $CaCO_3$, which is filtered out of the stream. The resulting $MgCl_2{\cdot}6H_2O$ 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 4681 kwh/tonne CO_2. 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 $MgCl_2.6H_2O$ causing it to break down into a HCl/H_2O vapor stream and a solid stream of Mg(OH)Cl. The HCl/H_2O 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:

$$MgCl_2.6H_2O + \Delta \rightarrow Mg(OH)Cl + 5\ H_2O\uparrow + HCl\uparrow \tag{41}$$

$$2\ Mg(OH)Cl(aq) \rightarrow Mg(OH)_2 + MgCl_2 \tag{42}$$

A $CaCl_2$ solution and a flue gas stream are added to the $Mg(OH)_2$ 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. Chemical reaction(s) occurring in this reactor include the following:

$$Mg(OH)_2 + CaCl_2 + CO_2 \rightarrow CaCO_3 \downarrow(s) + MgCl_2 + H_2O \tag{43}$$

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 4) are summarized below:

CASE 4
Combined Dehydration/Decomposition to Mg(OH)Cl

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

CO_2 Absorbed	53333	MTPY
$CaCl_2$	134574	MTPY
HCl Dry	88368	MTPY
$CaCO_3$	105989	MTPY
Hexahydrate recycled	492737	MTPY
DEHYDRATION & DECOMPOSITION TO 100% Mg(OH)Cl (250 °C) YEILDS 28.8% HCl VAPOR	5043	kWh/tonne CO2
	2.2	MW
Heat Recovery from 28% HCl vapor	361	kWh/tonne CO2
TOTAL	4681	kWh/tonne CO2

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

Process Stream Names →	$CaCl_2$	$CaCO_3$	FLUEGAS	H_2O	HCIVAP	$MgCl_2$	$MgCl_2$-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_2O	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_2O	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_2O	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_2O	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_2O	HClVAP	$MgCl_2$	$MgCl_2$-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_2O	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_2O	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_2O	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 $MgCl_2·6H_2O$

FIG. 10 shows a graph of the mass percentage of a heated sample of $MgCl_2·6H_2O$. 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 decompositional 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 $MgCl_2·6H_2O$, 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:

$$2\ Mg(OH)Cl\ (aq) \rightarrow Mg(OH)_2 + MgCl_2 \qquad (44)$$

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 Mg(OH)Cl = ½

Expected amount of $Mg(OH)_2$

$2\ Mg(OH)Cl\ (aq) \rightarrow Mg(OH)_2 + MgCl_2$

$3.016gm * (MW\ Mg(OH)_2 \div (MW\ Mg(OH)Cl * ½ = 1.1447\ gm$

Precipitate collected = 1.1245 gm

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

Analytical data:

Next the sample of $Mg(OH)_2$ 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 $Mg(OH)_2$ while the spikes at the bottom are those of MgO. Thus verifying that the recovered precipitate from the dissolution of Mg(OH)Cl has a signal resembling that of $Mg(OH)_2$.

```
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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 $Mg(OH)_2$ {or Mg(OH)Cl} and $CaCl_2$

Approximately 20 grams of $Mg(OH)_2$ was placed in a bubble column with two liters of water and CO_2 was bubbled though 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:

$$Mg(OH)_2 + CO_2 + CaCl_2 \rightarrow CaCO_3\downarrow + H_2O \tag{45}$$

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

EDS

```
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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 Mg(OH)Cl from the decomposition of $MgCl_2 \cdot 6H_2O$ was used instead of $Mg(OH)_2$. Although Mg(OH)Cl has half the hydroxide $[OH^-]$, as $Mg(OH)_2$ it is expected to absorb CO_2 and form precipitated $CaCO_3$ (PCC).

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

EDS

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

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

Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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

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 $(Mg,Fe)_2SiO_4$ and serpentine $Mg_3Si_2O_5(OH)_4$were crushed and 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.

Olivine Filtrate Reacted with HCl at Room Temperature

```
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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

```
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
```

```
  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
```

Serpentine Filtrate Reacted with HCl at Room Temperature

```
Note: Results do not include elements with Z<11 (Na).
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  Mg-K    0.1674   1.466   32.47   24.53    +/- 0.15
  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
  Total 100.00  100.00
```

Serpentine Filtrate Reacted with HCl at 70°C

```
Note: Results do not include elements with Z<11 (Na).
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  Mg-K    0.1759   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
  Total 100.00  100.00

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

The filtrate clearly for both minerals serpentine and olivine at ambient conditions and 70 °C all illustrate the presence of $MgCl_2$, and a small amount of $FeCl_2$ in the case of olivine.

Olivine Filtrand Reacted with HCl at Room Temperature

```
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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
  Total 100.00  100.00

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

Olivine Filtrand Reacted with HCl at 70 °C

```
Element  k-ratio    ZAF   Atom %  Element  Wt % Err.
  (calc.)  Wt %   (1-Sigma)
  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
   Total 100.00   100.00

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

Given that the formula for olivine is $(Mg,Fe)_2SiO_4$, 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 the chart), evidently more than 50% of the magnesium passed through the filter.

Serpentine Filtrand Reacted with HCl at Room Temperature

```
Element  k-ratio     ZAF   Atom %   Element   Wt % Err.
   (calc.)  Wt %    (1-Sigma)
   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
   Total 100.00   100.00

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

Serpentine Filtrand Reacted with HCl at 70 °C

```
Element  k-ratio     ZAF   Atom %   Element   Wt % Err.
   (calc.)  Wt %    (1-Sigma)
   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
   Total 100.00   100.00

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

Given that the formula of serpentine is $(Mg,Fe)_3Si_2O_5(OH)_4$ the initial 1.5:1 ratio of (Mg + Fe) to Si has been whittled down to (37 + 9.3:56.5) = 0.898:1.

Example 9B – Temperature/Pressure Simulation for Decomposition of MgCl2·6(H2O)

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 $MgCl_2 \cdot 6(H_2O)$. Inputs are:

1) $MgCl_2 \cdot 6H_2O$
2) $CaCl_2$
3) The temperature of the hot stream leaving the heat exchanger (HX) labeled Mg(OH)Cl (see FIGS. 7-8).
4) Percentage of Solids separated in decanter.
5) Water needed labeled H_2O
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 $MgCl_2{\cdot}6H_2O$ 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 ($MgCa(SiO_3)_2$) (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

($MgCO_3$) with Dolomite $CaMg(CO_3)_2$ 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 $MgCl_2$ to MgO and Mg(OH)Cl, respectively, are depicted below.

I) Ca-Mg Process

Overall reaction $CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$

a) Full decomposition ("the $CaSiO_3$-MgO process"):

1) $MgCl_2.6H_2O + \Delta \rightarrow MgO + 5H_2O\uparrow + 2HCl\uparrow$

A thermal decomposition reaction.

2) $2HCl(aq) + CaSiO_3 \rightarrow CaCl_2(aq) + SiO_2\downarrow + H_2O$

A rock melting reaction.

Note 5 H_2O will be present per 2 moles of HCl during the reaction.

3) $MgO + CaCl_2(aq) + CO_2 \rightarrow CaCO_3\downarrow + MgCl_2(aq)$

Some versions of this equation use $Mg(OH)_2$ which is formed from MgO and H_2O.

4) $MgCl_2(aq) + 6H_2O \rightarrow MgCl_2\cdot6H_2O$

Regeneration of $MgCl_2.6H_2O$, return to #1.

b) Partial decomposition ("the $CaSiO_3$-Mg(OH)Cl process"):

1) $2 \times [MgCl_2\cdot6H_2O + \Delta \rightarrow Mg(OH)Cl + 5H_2O\uparrow + HCl\uparrow]$

Thermal decomposition.

Twice as much $MgCl_2\cdot6H_2O$ is needed to trap the same amount of CO_2.

2) $2HCl(aq) + CaSiO_3 \rightarrow CaCl_2(aq) + SiO_2\downarrow + H_2O$

Rock melting reaction.

3) $2Mg(OH)Cl + CaCl_2(aq) + CO_2 \rightarrow CaCO_3\downarrow + 2MgCl_2(aq) + H_2O$

CO_2 capture reaction

4) $2 MgCl_2 + 12H_2O \rightarrow 2MgCl_2\cdot6H_2O$

Regeneration of $MgCl_2.6H_2O$, return to #1.

II) Mg Only Process

Overall reaction $MgSiO_3 + CO_2 \rightarrow MgCO_3 + SiO_2$

c) Full decomposition ("the $MgSiO_3$-MgO process")

1) $2HCl(aq) + MgSiO_3 + (x\text{-}1)H_2O \rightarrow MgCl_2 + SiO_2\downarrow + xH_2O$

Rock melting reaction.

2) $MgCl_2{\cdot}xH_2O + \Delta \rightarrow MgO + (x\text{-}1)H_2O\uparrow + 2HCl\uparrow$

Thermal decomposition reaction.

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

3) $MgO + CO_2 \rightarrow MgCO_3$

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 $MgSiO_3$-Mg(OH)Cl process")

1) $2HCl(aq) + MgSiO_3 \rightarrow MgCl_2 + SiO_2\downarrow + H_2O$

Rock melting reaction.

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

2) $2 \times [MgCl_2.xH_2O + \Delta \rightarrow Mg(OH)Cl + (x\text{-}1)\ H_2O\uparrow + HCl\uparrow]$

Decomposition.

Twice as much $MgCl_2{\cdot}(x\text{-}1)H_2O$ is needed to trap the same amount of CO_2.

3) $2Mg(OH)Cl + CO_2 \rightarrow MgCO_3\downarrow + MgCl_2 + H_2O$

CO_2 capture reaction.

4) $MgCl_2(aq) + 6H_2O \rightarrow MgCl_2{\cdot}6H_2O$

Regenerate $MgCl_2{\cdot}6H_2O$, 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 $MgCl_2{\cdot}6H_2O$ and $MgCl_2{\cdot}2H_2O$.

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: $\frac{1}{2}\,CaMg(SiO_3)_2 + CO_2 \rightarrow \frac{1}{2}\,CaMg(CO_3)_2 + SiO_2$

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

1) $MgCl_2.6H_2O + \Delta \rightarrow MgO + 5H_2O\uparrow + 2HCl\uparrow$

   Thermal decomposition.

2) $HCl + \frac{1}{2}\,CaMg(SiO_3)_2 \rightarrow \frac{1}{2}\,CaCl_2 + \frac{1}{2}\,MgSiO_3\downarrow + \frac{1}{2}\,SiO_2\downarrow + \frac{1}{2}\,H_2O$

   First rock melting reaction.

3) $HCl + \frac{1}{2}\,MgSiO_3 \rightarrow \frac{1}{2}MgCl_2 + \frac{1}{2}\,SiO_2\downarrow + \frac{1}{2}\,H_2O$

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

4) $MgO + \frac{1}{2}\,CaCl_2 + CO_2 \rightarrow \frac{1}{2}\,CaMg(CO_3)_2\downarrow + \frac{1}{2}\,MgCl_2$

5) $\frac{1}{2}\,MgCl_2 + 3H_2O \rightarrow \frac{1}{2}\,MgCl_2.6H2O$

   Regenerate $MgCl_2.6H_2O$, return to #1.

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

1) $2 \times [MgCl_2\cdot 6H_2O + \Delta \rightarrow Mg(OH)Cl + 5H_2O\uparrow + HCl\uparrow\,]$

   Thermal decomposition.

   Twice as much $MgCl_2\cdot 6H_2O$ is needed to trap the same amount of CO_2.

2) $HCl + \frac{1}{2}\,CaMg(SiO_3)_2 \rightarrow \frac{1}{2}\,CaCl_2 + \frac{1}{2}\,MgSiO_3\downarrow + \frac{1}{2}\,SiO_2\downarrow + \frac{1}{2}\,H_2O$

   First rock melting reaction.

3) $HCl + \frac{1}{2}\,MgSiO_3 \rightarrow \frac{1}{2}MgCl_2 + \frac{1}{2}\,SiO_2\downarrow + \frac{1}{2}\,H_2O$

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

4) $2Mg(OH)Cl + \frac{1}{2}\,CaCl_2 + CO_2 \rightarrow \frac{1}{2}\,CaMg(CO_3)_2\downarrow + 3/2\,MgCl_2 + H_2O$

5) $3/2\,MgCl_2 + 9H_2O \rightarrow 3/2\,MgCl_2\cdot 6H_2O$

   Regenerate $MgCl_2\cdot 6H_2O$, 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 CO_2 percentage of flue gas 7.2% - 18% includes models run at 7.2%, 10%, 14% and 18% respectively.

Calcium Silicate process:

The $CaSiO_3$-MgO and $CaSiO_3$-Mg(OH)Cl decomposition processes are further divided into two stages, the first step consists of a dehydration reaction where $MgCl_2{\cdot}6H_2O$ is converted to $MgCl_2{\cdot}2H_2O$ + 4 H_2O and the second step in which the $MgCl_2{\cdot}2H_2O$ is converted to Mg(OH)Cl + HCl + H_2O if partial decomposition is desired or required and MgO + 2HCl + H_2O if total decomposition is desired or required. FIG. 15 describes a layout of this process.

Magnesium Silicate process:

The $MgSiO_3$-MgO and $MgSiO_3$-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 $MgCl_2{\cdot}2H_2O$ 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 HCl + silicate", and then moves to the "decomposition reaction ($MgCl_2$ + 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 $MgCl_2{\cdot}6H_2O + \Delta \rightarrow MgCl_2{\cdot}2H_2O + 4\ H_2O$ followed by the decomposition reaction $MgCl_2{\cdot}2H_2O + \Delta \rightarrow MgO + 2HCl + H_2O$ (full decomposition) or $MgCl_2{\cdot}2H_2O + \Delta \rightarrow Mg(OH)Cl + HCl + H_2O$ partial decomposition. FIG. 17 describes a layout of this process.

The ensuing HCl from the decomposition then reacts with the Diopside $CaMg(SiO_3)_2$ in a two step "rock melting reaction." The first reaction creates $CaCl_2$ through the reaction $2HCl + CaMg(SiO_3)_2 \rightarrow CaCl_2(aq) + MgSiO_3\downarrow + SiO_2\downarrow + H_2O$. The solids from the previous reaction are then reacted with HCl a second time to produce $MgCl_2$ through the reaction $MgSiO_3 + 2HCl \rightarrow MgCl_2 + SiO_2\downarrow + H_2O$. 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% CO_2 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 CO_2 content of this gas is 10% by weight. This amount of CO_2 is the basis for examples 10 through 21 which is:

Amount of CO_2 present in the flue gas per year:

136,903,680 tons per year * 10% = 13,690,368 tons per year

Amount of CO_2 absorbed per year.

13,690,368 tons per year * 50% = 6,845,184 tons per year of CO_2.

Since the amount of CO_2 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 $CaSiO_3$-MgO and the $CaSiO_3$-Mg(OH)Cl process (examples 10-13) the overall reaction is:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

For all the examples of both the $MgSiO_3$-MgO and the $MgSiO_3$-Mg(OH)Cl process (examples 14-17) the overall reaction is:

$$MgSiO_3 + CO_2 \rightarrow MgCO_3 + SiO_2$$

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

$$\frac{1}{2} CaMg(SiO_3)_2 + CO_2 \rightarrow \frac{1}{2} CaMg(CO_3)_2 + SiO_2$$

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 CO_2 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 CO_2 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

* Number of moles must be divided by 2 to measure comparable CO_2 absorption with the other processes,

For Examples 10-13:

The $CaSiO_3$ consumption is:

6,845,184 tons per year * (116.16 / 44.01) = 18,066,577 tons per year.

The $CaCO_3$ production is:

6,845,184 tons per year * (100.09 / 44.01) = 15,559,282 tons per year.

The SiO_2 production is:

6,845,184 tons per year * (60.08 / 44.01) = 9,344,884 tons per year

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 CO_2 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 CO_2 absorption).

HEAT BALANCE						
Process	**$CaSiO_3$-Mg(OH)Cl**	**$CaSiO_3$-MgO**	**$MgSiO_3$-Mg(OH)Cl**	**$MgSiO_3$-MgO**	**Diop.-Mg(OH)Cl**	**Diop.-MgO**
Examples	**10,11**	**12,13**	**14,15**	**16,17**	**18,19**	**20,21**
Dehydration Chamber (MW)	2670	1087	n/a	n/a	2614	1306
HEX TO DI(210 °C)						
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 CO_2 captured as a function of flue gas temperature and CO_2 concentration. Examples 10 through 13.

Process	**$CaSiO_3$-Mg(OH)Cl**					**$CaSiO_3$ - MgO**	**$CaSiO_3$ - Mg(OH)Cl**	**$CaSiO_3$ - MgO**
Flue Gas Source/Temp.	**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 CO_2 captured for varying CO_2 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 $CaSiO_3$-Mg(OH)Cl and $CaSiO_3$-MgO processes.

Table 14. Percentage CO_2 captured as a function of flue gas temperature and CO_2 concentration. Examples 14 through 17.

Process	$MgSiO_3$-Mg(OH)Cl					$MgSiO_3$ - MgO	$MgSiO_3$ - Mg(OH)Cl	$MgSiO_3$ - MgO
Flue Gas Source/Temp.	**Coal 320 °C**	**Coal 360 °C**	**Coal 400 °C**	**Coal 440 °C**	**Coal 550 °C**	**Coal 550 °C**	**Ngas 600 °C**	**Ngas 600 °C**
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 CO_2 captured for varying CO_2 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 $MgSiO_3$-Mg(OH)Cl and $MgSiO_3$-MgO processes.

Table 15. Percentage CO_2 captured as a function of flue gas temperature and CO_2 concentration. Examples 18 through 21.

Process	**Diopside-Mg(OH)Cl**					**Diop - MgO**	**Diop - Mg(OH)Cl**	**Diop - MgO**
Flue Gas Source/Temp.	**Coal 320 °C**	**Coal 360 °C**	**Coal 400 °C**	**Coal 440 °C**	**Coal 550 °C**	**Coal 550 °C**	**Ngas 600 °C**	**Ngas 600 °C**
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 CO_2 captured for varying CO_2 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_2O	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_2O	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_2O	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
$CO3^{2-}$	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_2O	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
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

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_2O	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_2O	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_2O	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_2O	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
$Mg(OH)_2$	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_2O	H_2O	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_2O	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_2O**	**H_2O**	**HCl Vapor**	**$MgCl_2$--2**	**$MgCl_2$-2w**	**$MgCl_2$-Si**
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
$MgCl_2$*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_2O	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
$CO3^{2-}$	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_2O	H_2O	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 VFrac	1	0	0.004	1	0	0	0
Mass SFrac	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_2O	H_2O	HCl Vapor	$MgCl_2$--2	$MgCl_2$-2w	$MgCl_2$-Si
H_2O	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_2O	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
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
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	FLUEGAS	H_2O	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+07	3.94E+07	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+07	0.001	1.82E+07	1.82E+07	11.834	1.02E+07	1866.916	9636.543

Process Stream Names →	**5**	**$CaCl_2$-2W**	**FLUEGAS**	**H_2O**	**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_2O	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	FLUEGAS	H_2O	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	11965.659	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
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-	SiO_2	SLURRY	SOLIDS	SOLIDS-1	SOLIDS-2	VENT
PH							5.163			6.252	
Temperature °C	25	100	100	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
Mass VFrac	0	0	0	0	0	0	0	0	0	0	1
Mass SFrac	1	0	1	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	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	2804.199	1607.827	185622	2276.765	3828.933	8017.333	5.85E+07
Enthalpy MW	-7167.458	0	-16601.2	-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	160.371	165.327	29.855	178.921	177.393	120.2	0.06
H_2O	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

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
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

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

Process Stream Names →	5	$CaCl_2$-2W	FLUEGAS	H_2O	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	-.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_2O	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	8.41.E+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_2O**	**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 →	MgCaSiO3	$MgCl_2$--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_2O	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			

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 $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2} O_2$
$Mg(NO_3)_2$	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 $Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + \frac{1}{2} O_2$
$Ca(NO_3)_2$	600	50	61% decomposition
$Ca(NO_3)_2$	600	Overnight	100% decomposition
LiCl	450	120	~0% decomposition

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 CO_2 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.

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 CO_2, includes CO_2 for process-required heat.

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

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 CO_2, which includes CO_2 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	3					
MW of Heat		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	4					
MW of Heat		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	2					
MW of Heat		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	2					
MW of Heat		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 CO_2 gas.

$CaCl_2(aq) + CO_2 + Mg(OH)_2 \Rightarrow MgCl_2(aq) + CaCO_3\downarrow + H_2O$

In order to optimize production of $Mg(OH)_2$, upon conversion of $MgCl_2$ 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 $MgCl_2$ 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 (H_2O) in the reaction below, does not become part of the products, it merely solvates the Mg^{2+} and Cl^- so they become an ionic solution.

$Mg(OH)Cl\ (H_2O) \Rightarrow \frac{1}{2} Mg(OH)_2\downarrow + \frac{1}{2} MgCl_2(aq)$

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 $MgCl_2{\cdot}6H_2O$ instead of $MgCl_2(aq)$. The equation would be as follows:

$Mg(OH)Cl + 3H_2O \Rightarrow \frac{1}{2} Mg(OH)_2\downarrow + \frac{1}{2} MgCl_2.6H_2O$

Thus, by maintaining a $MgCl_2$ to water ratio of greater than or equal to 6 to 1, production of aqueous $MgCl_2$ and solid $Mg(OH)_2$ is favored. Thus, an example set of CO_2 capture reactions can be represented as:

i) $MgCl_2{\cdot}H_2O \Rightarrow Mg(OH)CL + H_2O + HCl$

ii) $HCl + CaSiO_3 \Rightarrow CaCl_2 + H_2O + SiO_2$

iii) $Mg(OH)Cl + MgCl_2 + H_2O \Rightarrow Mg(OH)_2 + MgCl_2 + H_2O$

iv) $H_2O + Mg(OH)_2 + CO_2 + CaCl_2 \Rightarrow MgCl_2 + CaCO_3 + H_2O$

With an overall reaction of: $CaSiO_3\ CO_2 \Rightarrow CaCO_3 + SiO_2$.

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 $MgCl_2$ 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 ($MgCl_2.6H_2O$ almost) and stream SOLIDS-2, which is the $Mg(OH)_2$ heading to the absorption column.

* * * * * * * * * * * * * * * *

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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U.S. Prov. Appln. 60/642,698
U.S. Prov. Appln. 60/718,906
U.S. Prov. Appln. 60/973,948
U.S. Prov. Appln. 61/032,802
U.S. Prov. Appln. 61/033,298
U.S. Prov. Appln. 61/288,242
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U.S. Patent 7,727,374

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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; also available at http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/carbon_seq01.html.

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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 $MgCl_2{\cdot}6H_2O$.

9. The method according to any one of claims 1-8, wherein the $MgCl_2$ of step (a) is greater than 90% by weight $MgCl_2{\cdot}6(H_2O)$.

10. The method according to any one of claims 1-9, wherein the first step (a) product comprises greater than 90% by weight $Mg(OH)Cl$.

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 $Mg(OH)_2$ product of step (b) is a solid and wherein separating the step (b) products comprises separating some or all of the solid $Mg(OH)_2$ 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 ($CaMg[Si_2O_6]$) or tremolite $Ca_2Mg_5\{[OH]Si_4O_{11}\}_2$.

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 ($Fe_2[SiO_4]$).

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.

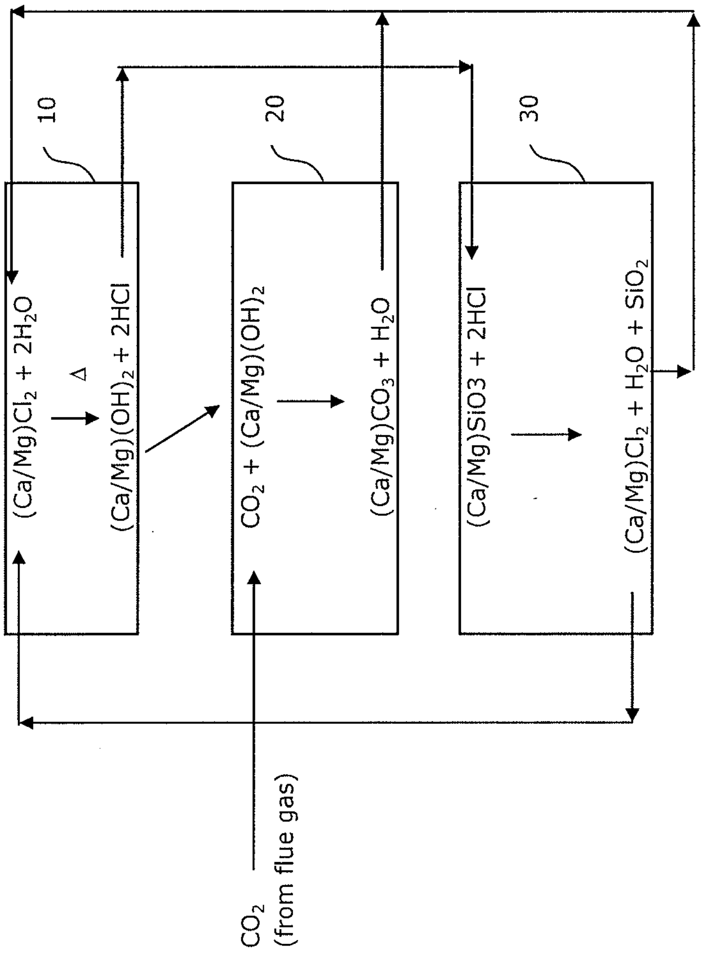
10
20
30
$(Ca/Mg)Cl_2 + 2H_2O$
$\xrightarrow{\Delta}$
$(Ca/Mg)(OH)_2 + 2HCl$
$CO_2 + (Ca/Mg)(OH)_2$
$\rightarrow$
$(Ca/Mg)CO_3 + H_2O$
$(Ca/Mg)SiO3 + 2HCl$
$\rightarrow$
$(Ca/Mg)Cl_2 + H_2O + SiO_2$
CO_2
(from flue gas)

FIG. 1

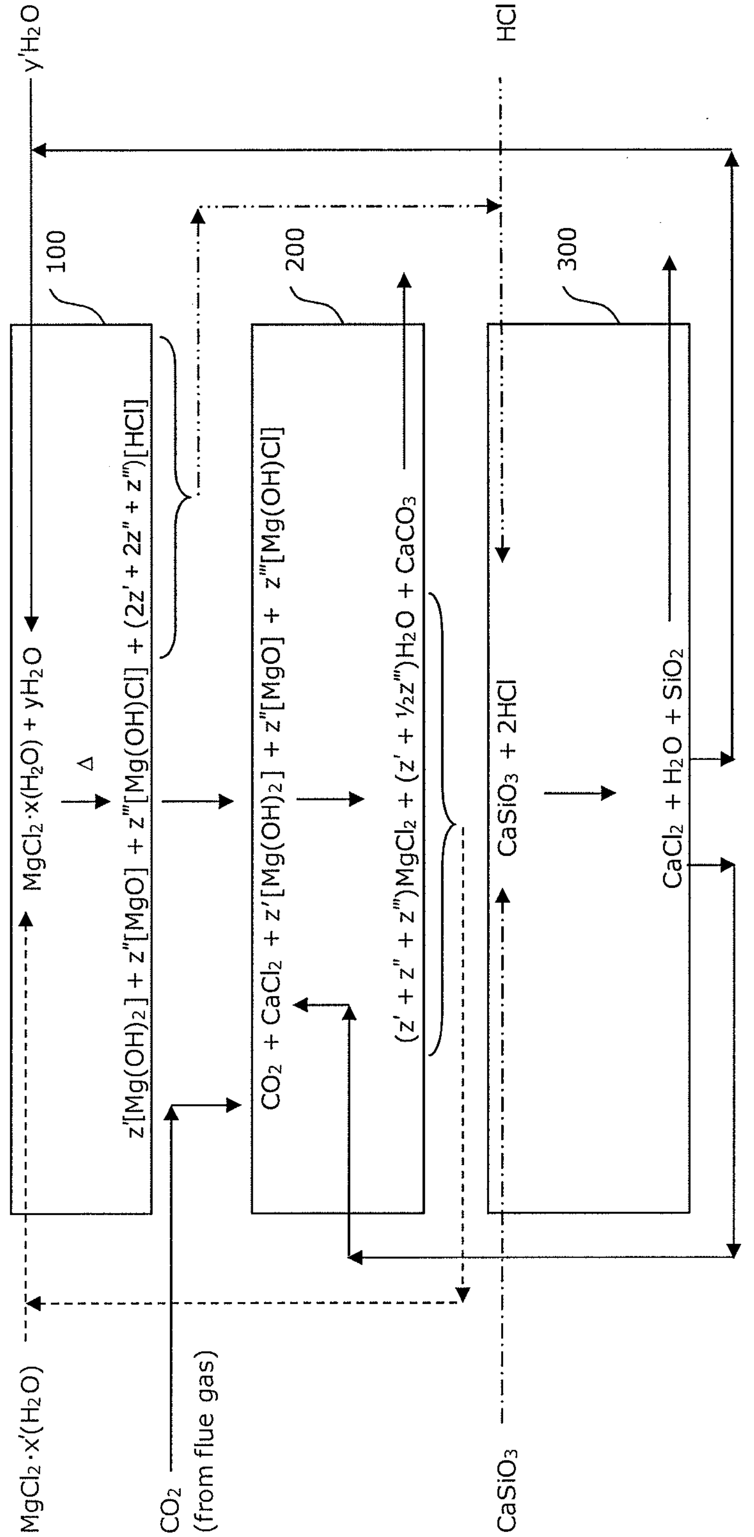
$y'H_2O$
HCl
100
200
300
$MgCl_2 \cdot x(H_2O) + yH_2O \xrightarrow{\Delta}$
$z'[Mg(OH)_2] + z''[MgO] + z'''[Mg(OH)Cl] + (2z' + 2z'' + z''')[HCl]$
$CO_2 + CaCl_2 + z'[Mg(OH)_2] + z''[MgO] + z'''[Mg(OH)Cl]$
$(z' + z'' + z''')MgCl_2 + (z' + \frac{1}{2}z''')H_2O + CaCO_3$
$CaSiO_3 + 2HCl$
$CaCl_2 + H_2O + SiO_2$
$MgCl_2 \cdot x'(H_2O)$
CO_2 (from flue gas)
$CaSiO_3$

FIG. 2

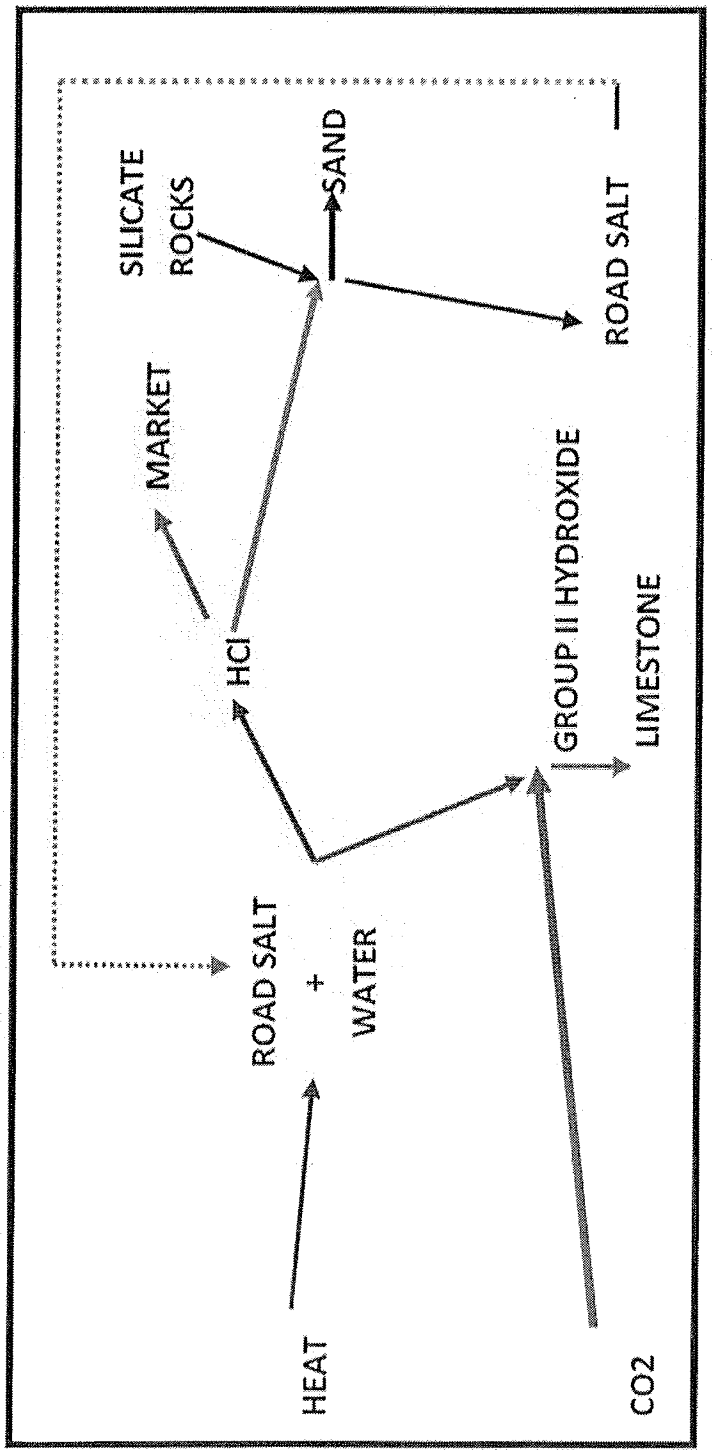
HEAT
CO2
ROAD SALT
+
WATER
HCl
GROUP II HYDROXIDE
LIMESTONE
MARKET
SILICATE
ROCKS
SAND
ROAD SALT

FIG. 3

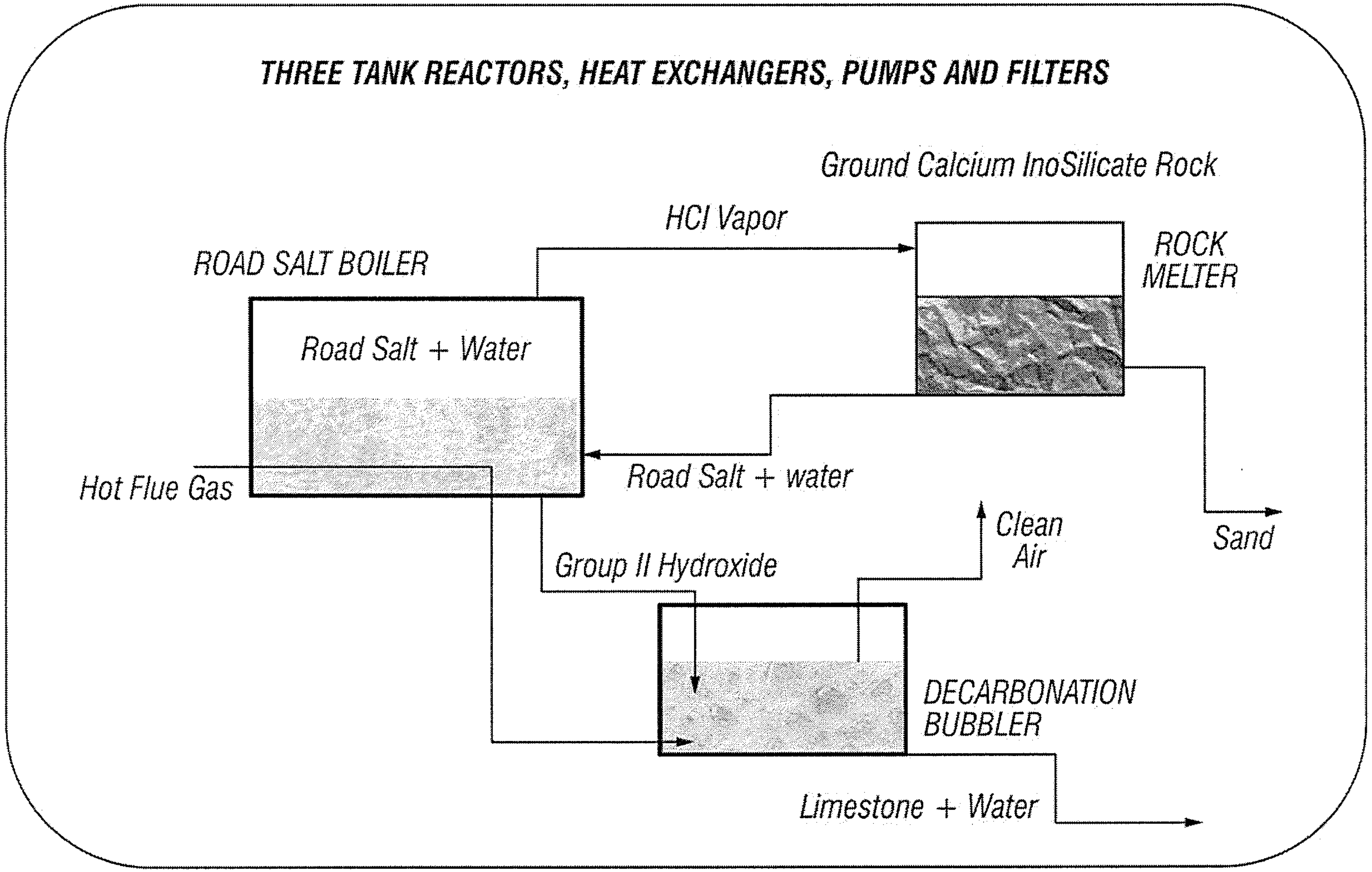
THREE TANK REACTORS, HEAT EXCHANGERS, PUMPS AND FILTERS
Ground Calcium InoSilicate Rock
HCl Vapor
ROAD SALT BOILER
ROCK MELTER
Road Salt + Water
Hot Flue Gas
Road Salt + water
Clean Air
Sand
Group II Hydroxide
DECARBONATION BUBBLER
Limestone + Water

FIG. 4

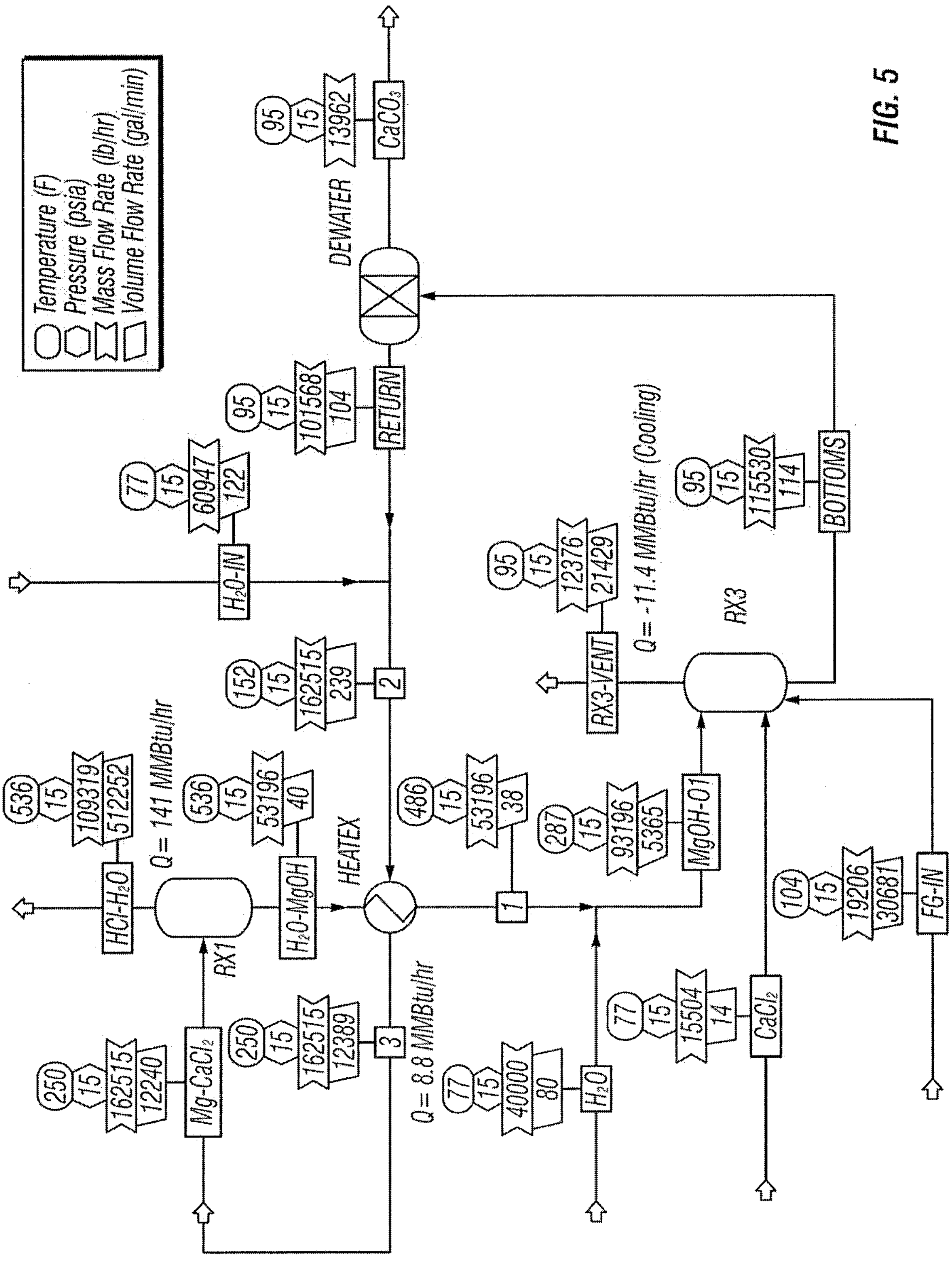
Temperature (F)
Pressure (psia)
Mass Flow Rate (lb/hr)
Volume Flow Rate (gal/min)
Mg-CaCl₂
250
15
162515
12240
RX1
HCl-H₂O
536
15
109319
512252
Q= 141 MMBtu/hr
H₂O-MgOH
536
15
53196
40
HEATEX
3
250
15
162515
12389
Q= 8.8 MMBtu/hr
1
486
15
53196
38
2
152
15
162515
239
H₂O-IN
77
15
60947
122
RETURN
95
15
101568
104
DEWATER
CaCO₃
95
15
13962
H₂O
77
15
40000
80
MgOH-01
287
15
93196
5365
CaCl₂
77
15
15504
14
FG-IN
104
15
19206
30681
RX3
RX3-VENT
95
15
12376
21429
Q= -11.4 MMBtu/hr (Cooling)
BOTTOMS
95
15
115530
114

FIG. 5

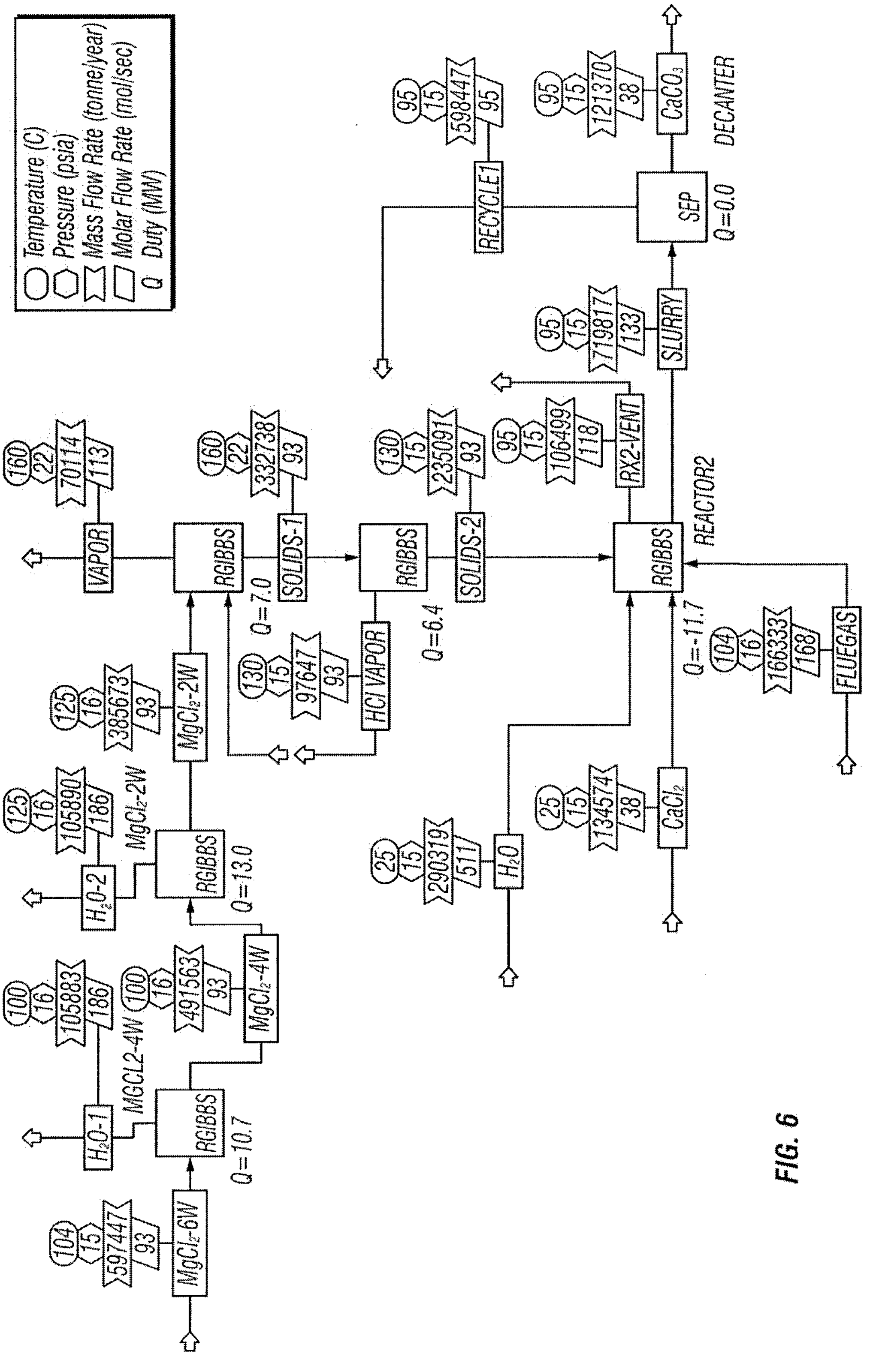
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Q Duty (MW)
MgCl2-6W
104
15
597447
93
RGIBBS
Q=10.7
H2O-1
MGCL2-4W
100
16
105883
186
MgCl2-4W
100
16
491563
93
RGIBBS
Q=13.0
H2O-2
MgCl2-2W
125
16
105890
186
MgCl2-2W
125
16
385673
93
RGIBBS
Q=7.0
VAPOR
160
22
70114
113
SOLIDS-1
160
22
332738
93
HCl VAPOR
130
15
97647
93
RGIBBS
Q=6.4
SOLIDS-2
130
15
235091
93
H2O
25
15
290319
511
CaCl2
25
15
134574
38
FLUEGAS
104
16
166333
168
RGIBBS
Q=-11.7
REACTOR2
RX2-VENT
95
15
106499
118
SLURRY
95
15
719817
133
SEP
Q=0.0
RECYCLE1
95
15
598447
95
CaCO3
95
15
121370
38
DECANTER

FIG. 6

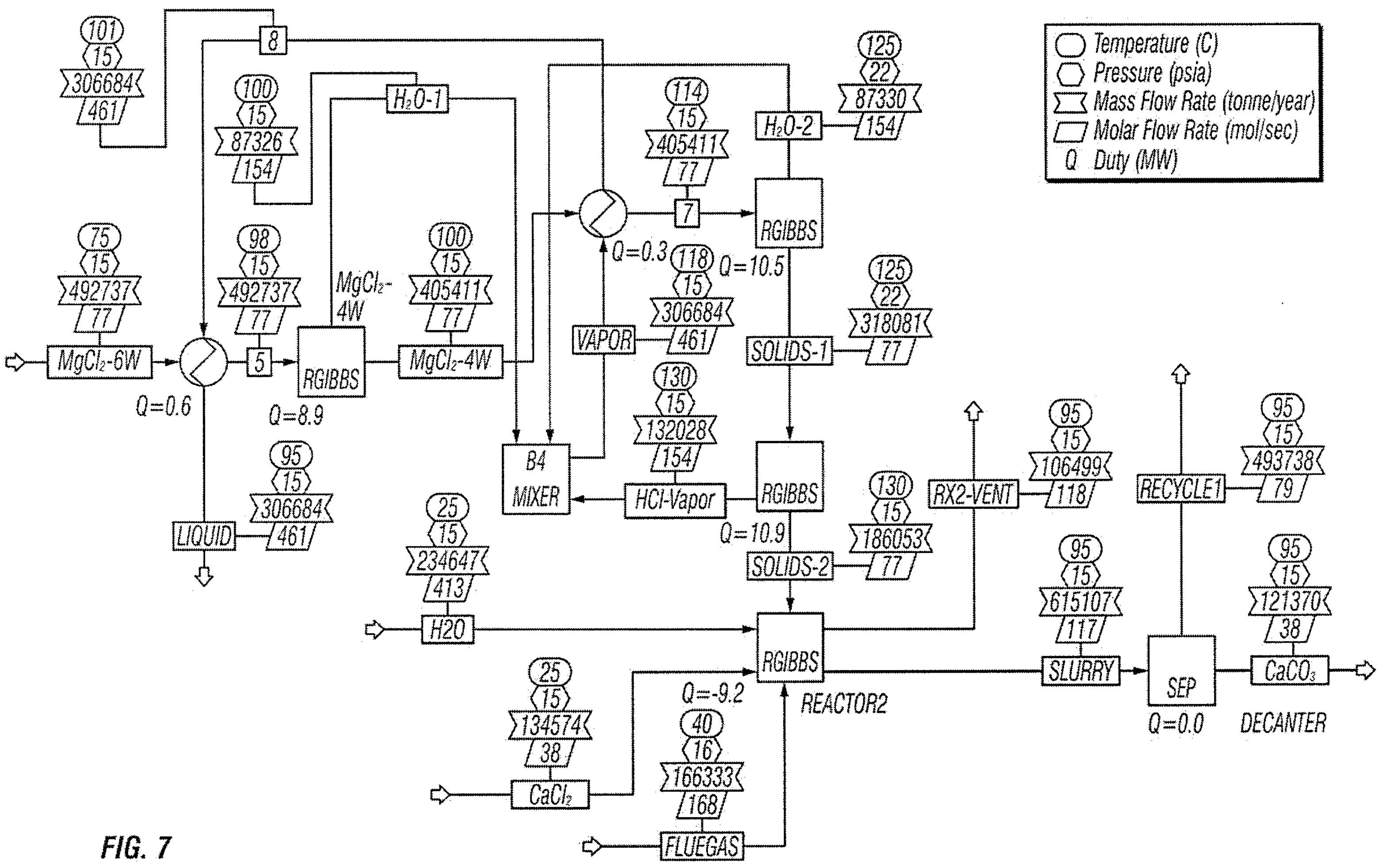
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Q Duty (MW)
101
15
306684
461
8
100
15
87326
154
H₂O-1
75
15
492737
77
MgCl₂-6W
Q=0.6
98
15
492737
77
5
RGIBBS
Q=8.9
MgCl₂-4W
100
15
405411
77
MgCl₂-4W
95
15
306684
461
LIQUID
B4 MIXER
VAPOR
118
15
306684
461
Q=0.3
114
15
405411
77
7
RGIBBS
Q=10.5
H₂O-2
125
22
87330
154
SOLIDS-1
125
22
318081
77
130
15
132028
154
HCl-Vapor
RGIBBS
Q=10.9
SOLIDS-2
130
15
186053
77
25
15
234647
413
H20
RGIBBS
REACTOR2
Q=-9.2
25
15
134574
38
CaCl₂
40
16
166333
168
FLUEGAS
RX2-VENT
95
15
106499
118
SLURRY
95
15
615107
117
SEP
Q=0.0
RECYCLE1
95
15
493738
79
CaCO₃
95
15
121370
38
DECANTER

FIG. 7

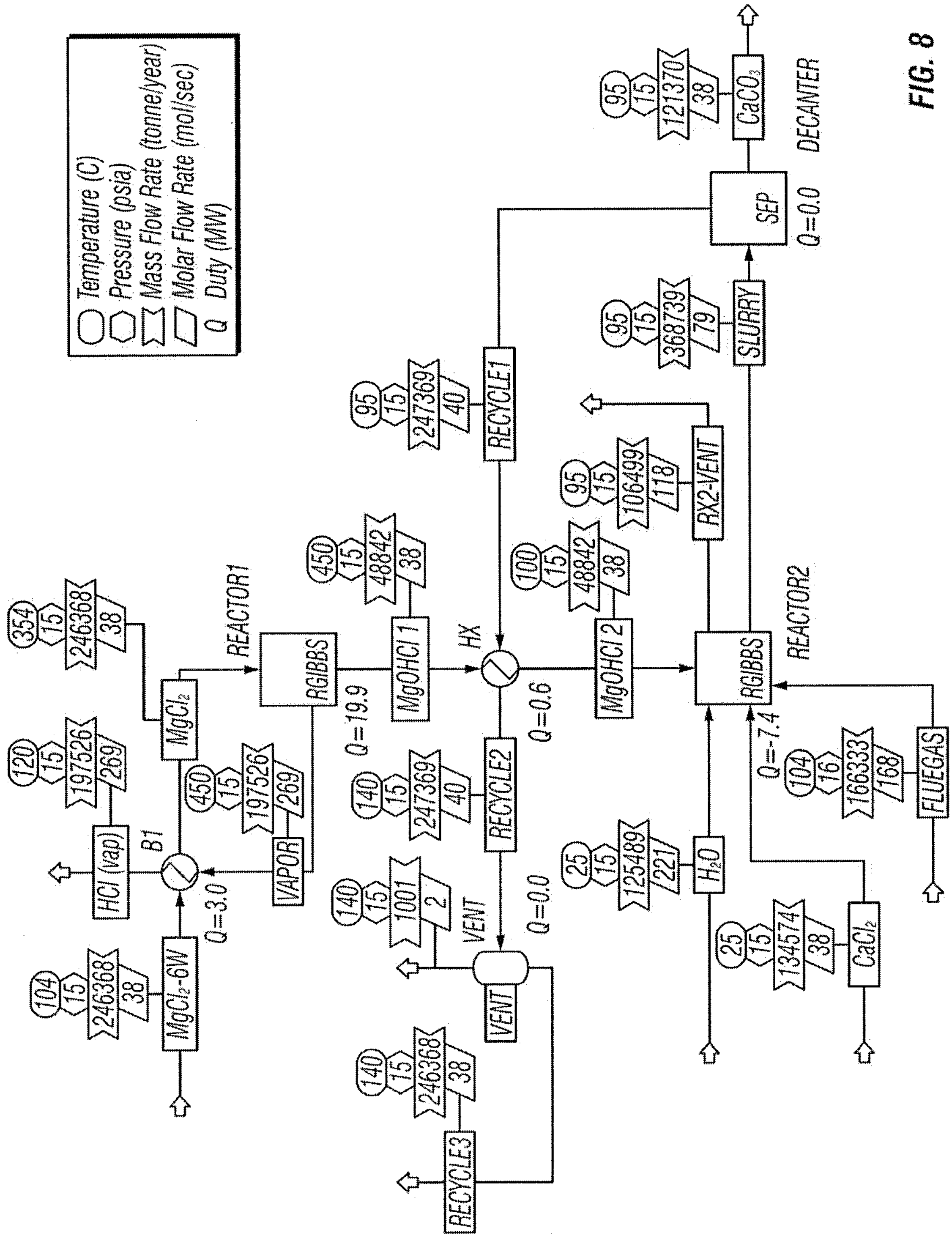
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Q Duty (MW)
MgCl₂-6W
104 15 246368 38
B1
Q=3.0
HCl (vap)
120 15 197526 269
MgCl₂
354 15 246368 38
VAPOR
450 15 197526 269
REACTOR1
RGIBBS
Q=19.9
MgOHCl 1
450 15 48842 38
HX
Q=0.6
MgOHCl 2
100 15 48842 38
RECYCLE1
95 15 247369 40
RECYCLE2
140 15 247369 40
VENT
Q=0.0
VENT
140 15 1001 2
RECYCLE3
140 15 246368 38
H₂O
25 15 125489 221
CaCl₂
25 15 134574 38
FLUEGAS
104 16 166333 168
REACTOR2
RGIBBS
Q=-7.4
RX2-VENT
95 15 106499 118
SLURRY
95 15 368739 79
SEP
Q=0.0
DECANTER
CaCO₃
95 15 121370 38

FIG. 8

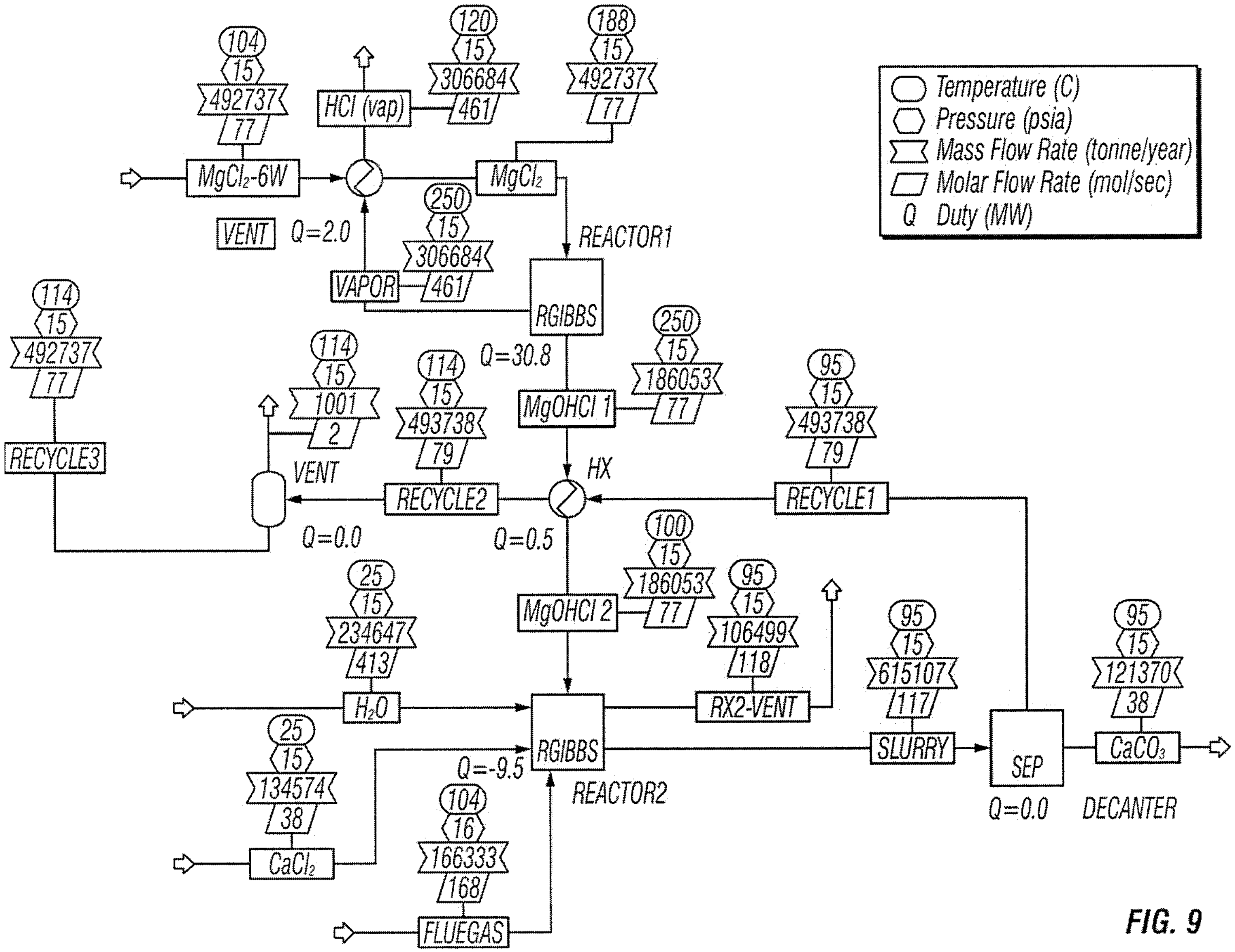
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Q Duty (MW)
104
15
492737
77
MgCl₂-6W
VENT
Q=2.0
120
15
306684
461
HCl (vap)
188
15
492737
77
MgCl₂
250
15
306684
461
VAPOR
REACTOR1
RGIBBS
Q=30.8
250
15
186053
77
MgOHCl 1
114
15
492737
77
RECYCLE3
114
15
1001
2
VENT
Q=0.0
114
15
493738
79
RECYCLE2
HX
Q=0.5
95
15
493738
79
RECYCLE1
100
15
186053
77
MgOHCl 2
25
15
234647
413
H₂O
25
15
134574
38
CaCl₂
104
16
166333
168
FLUEGAS
RGIBBS
Q=-9.5
REACTOR2
95
15
106499
118
RX2-VENT
95
15
615107
117
SLURRY
SEP
Q=0.0
95
15
121370
38
CaCO₃
DECANTER

FIG. 9

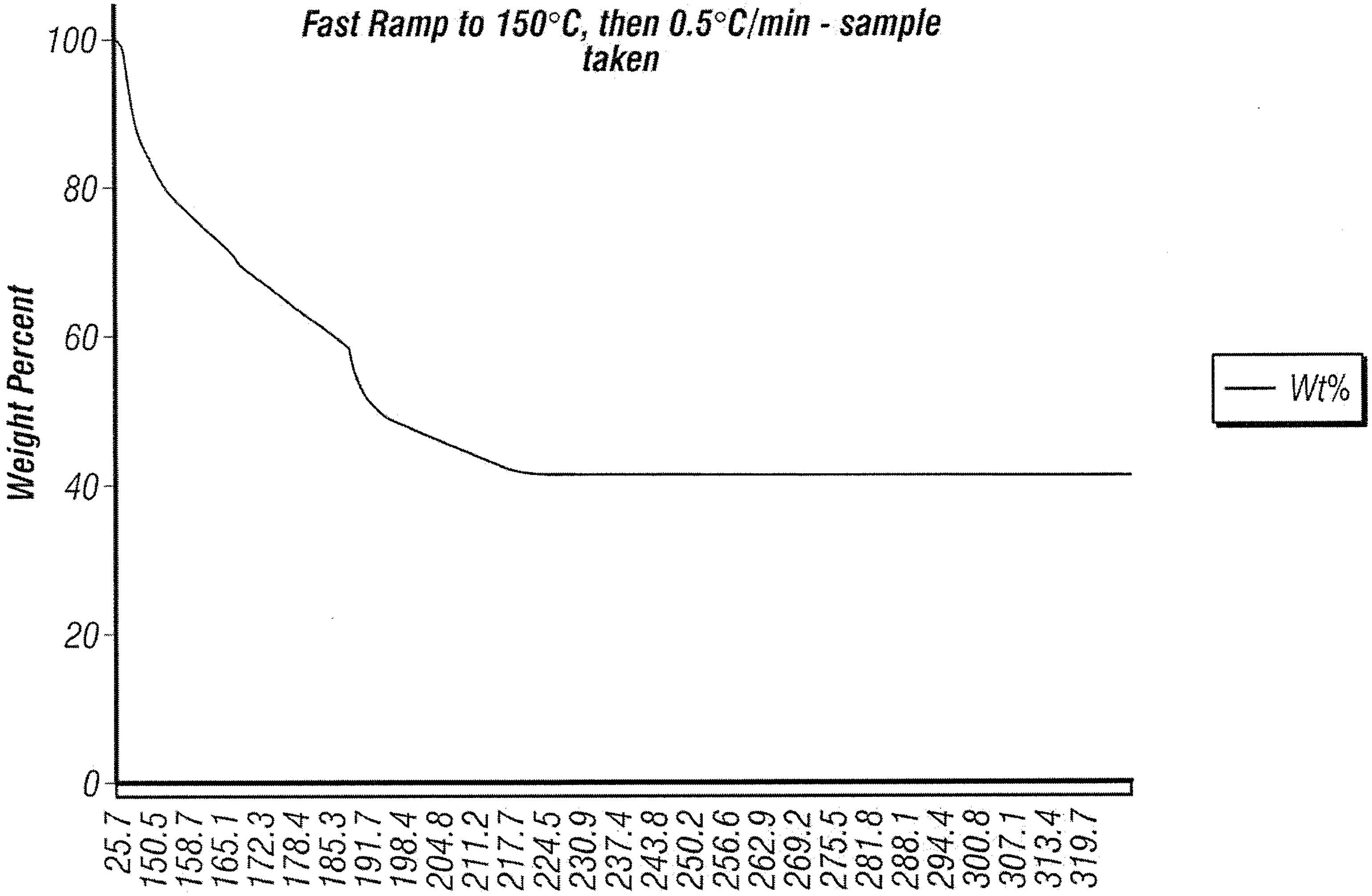
Fast Ramp to 150°C, then 0.5°C/min - sample taken
Weight Percent
100
80
60
40
20
0
Wt%
25.7
150.5
158.7
165.1
172.3
178.4
185.3
191.7
198.4
204.8
211.2
217.7
224.5
230.9
237.4
243.8
250.2
256.6
262.9
269.2
275.5
281.8
288.1
294.4
300.8
307.1
313.4
319.7
Temperature (°C)

FIG. 10

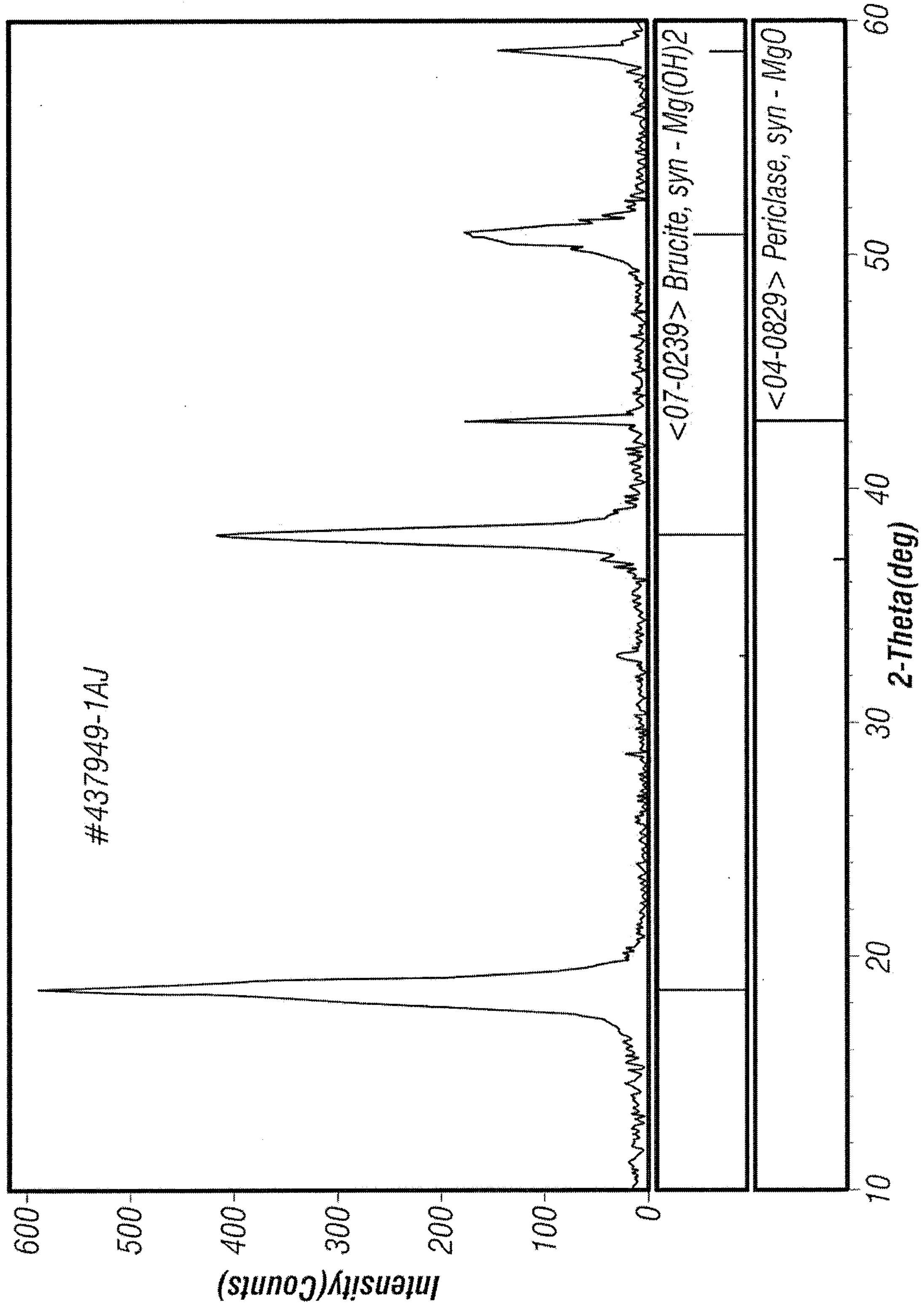
#437949-1AJ
Intensity(Counts)
600
500
400
300
200
100
0
<07-0239> Brucite, syn - Mg(OH)2
<04-0829> Periclase, syn - MgO
10
20
30
40
50
60
2-Theta(deg)

FIG. 11

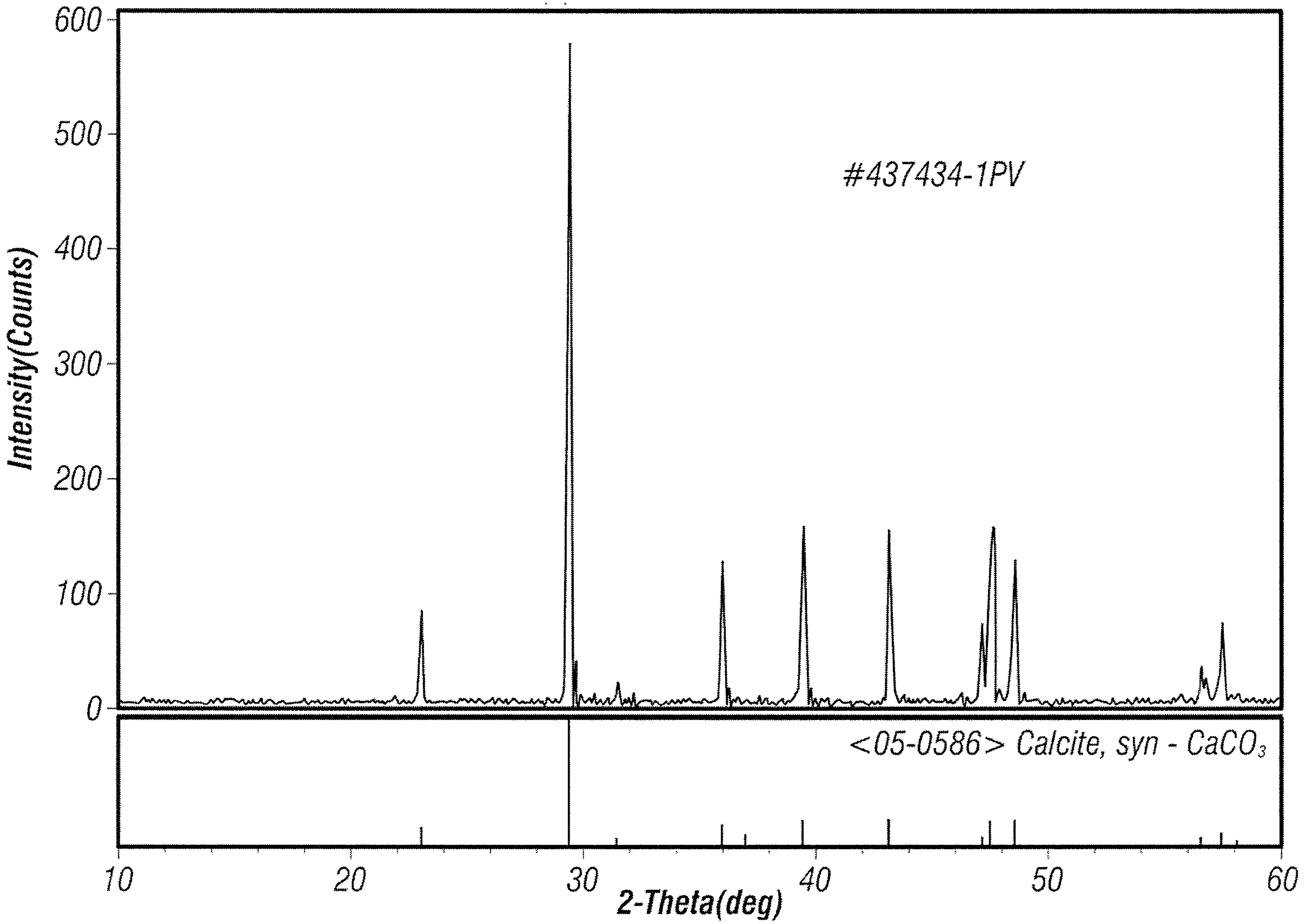
Intensity(Counts)
600
500
400
300
200
100
0
#437434-1PV
<05-0586> Calcite, syn - CaCO₃
10
20
30
40
50
60
2-Theta(deg)

FIG. 12

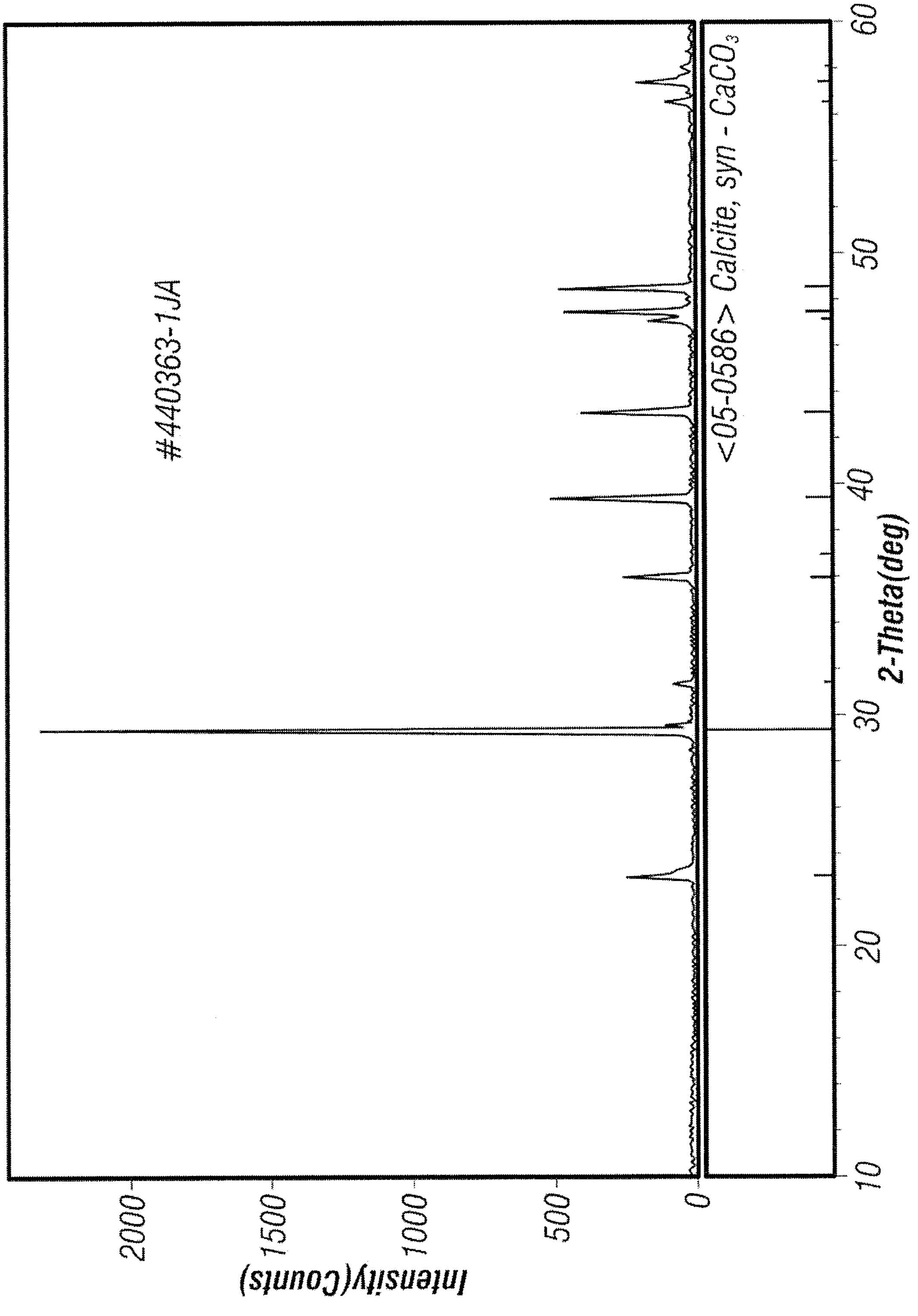
#440363-1JA
<05-0586> Calcite, syn - $CaCO_3$
Intensity(Counts)
2000
1500
1000
500
0
10
20
30
40
50
60
2-Theta(deg)

FIG. 13

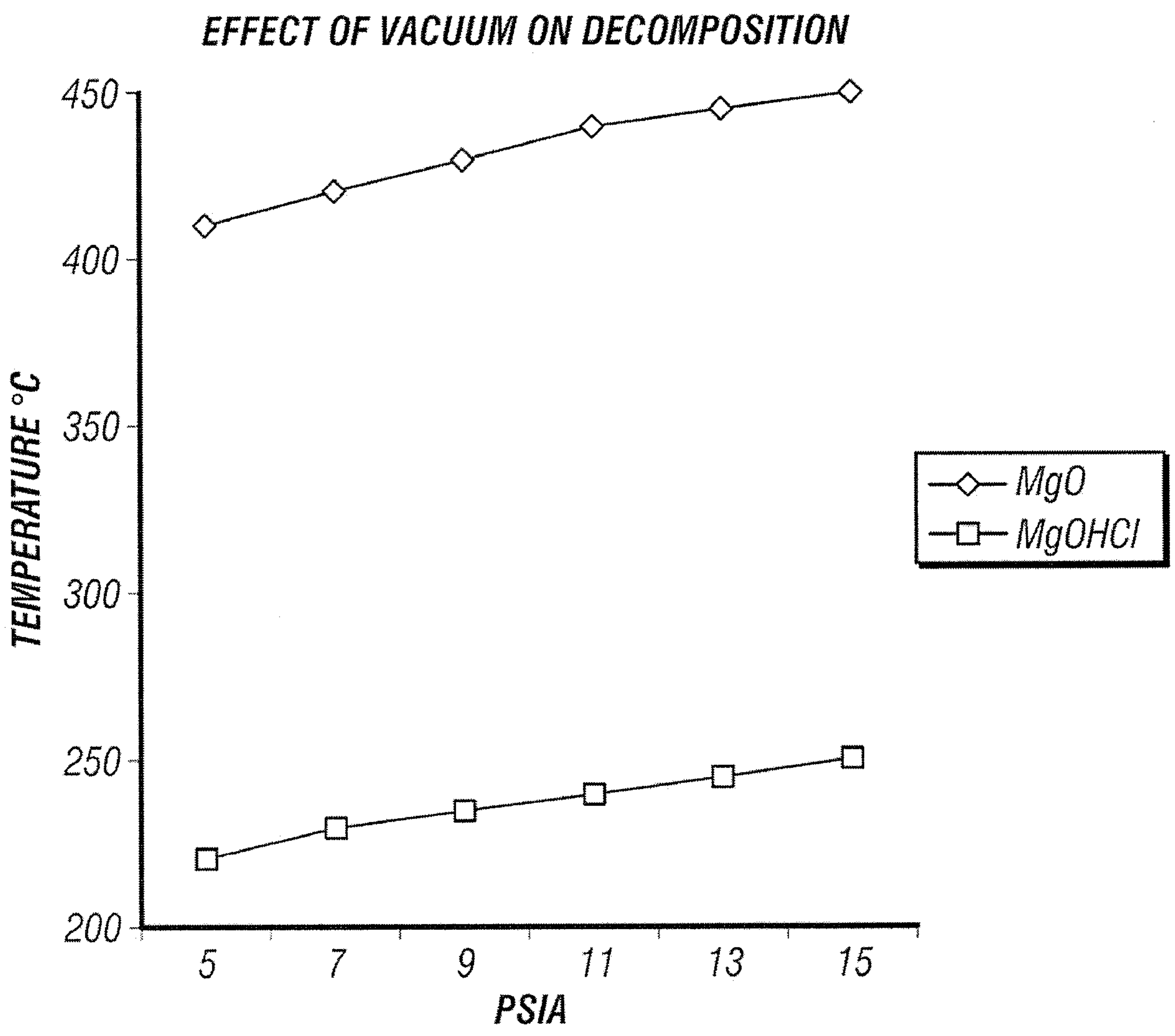
EFFECT OF VACUUM ON DECOMPOSITION
TEMPERATURE °C
450
400
350
300
250
200
5
7
9
11
13
15
PSIA
MgO
MgOHCl

FIG. 14

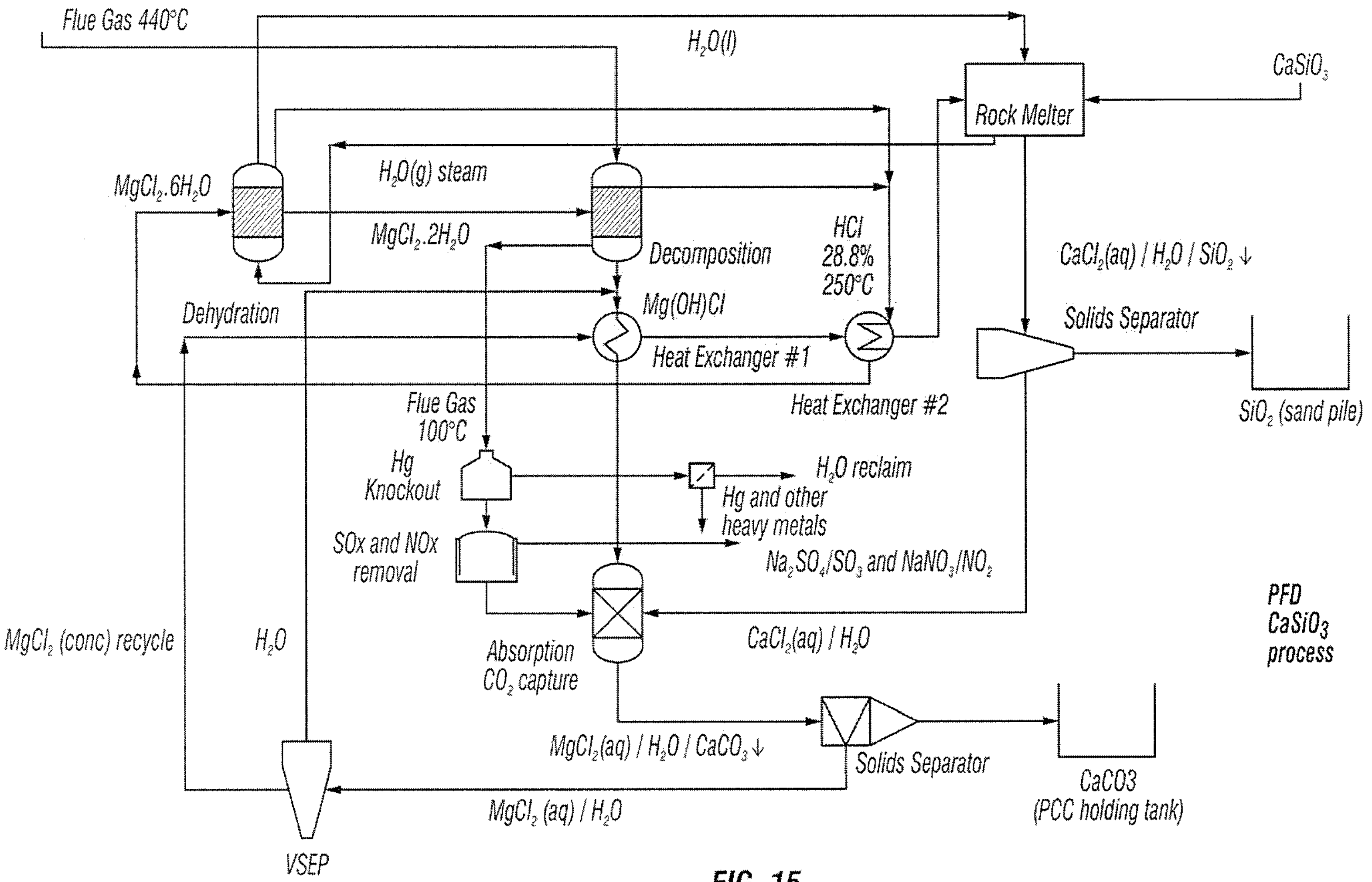
Flue Gas 440°C
$H_2O(l)$
$CaSiO_3$
Rock Melter
$MgCl_2.6H_2O$
$H_2O(g)$ steam
$MgCl_2.2H_2O$
Decomposition
HCl
28.8%
250°C
$CaCl_2(aq) / H_2O / SiO_2$ ↓
Dehydration
$Mg(OH)Cl$
Solids Separator
Heat Exchanger #1
Heat Exchanger #2
SiO_2 (sand pile)
Flue Gas
100°C
Hg
Knockout
H_2O reclaim
Hg and other
heavy metals
SOx and NOx
removal
Na_2SO_4/SO_3 and $NaNO_3/NO_2$
PFD
$CaSiO_3$
process
$MgCl_2$ (conc) recycle
H_2O
Absorption
CO_2 capture
$CaCl_2(aq) / H_2O$
$MgCl_2(aq) / H_2O / CaCO_3$ ↓
Solids Separator
CaCO3
(PCC holding tank)
$MgCl_2$ (aq) / H_2O
VSEP

FIG. 15

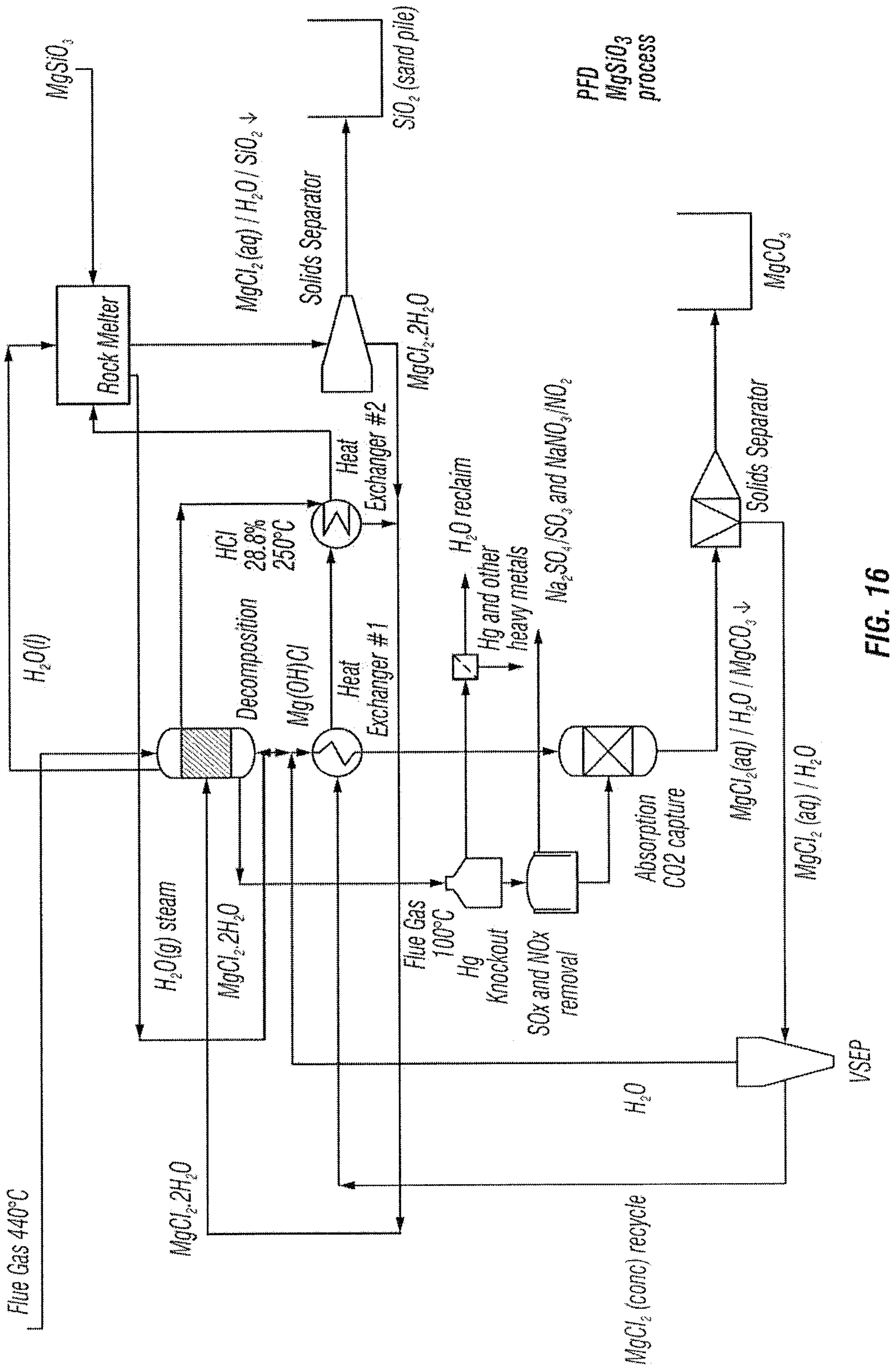
MgSiO3
Rock Melter
Solids Separator
MgCl2(aq) / H2O / SiO2 ↓
SiO2 (sand pile)
PFD
MgSiO3
process
MgCl2.2H2O
H2O(l)
Decomposition
HCl
28.8%
250°C
Heat
Exchanger #2
Mg(OH)Cl
Heat
Exchanger #1
H2O reclaim
Hg and other
heavy metals
Na2SO4/SO3 and NaNO3/NO2
Solids Separator
MgCO3
MgCl2(aq) / H2O / MgCO3 ↓
MgCl2 (aq) / H2O
Absorption
CO2 capture
H2O(g) steam
MgCl2.2H2O
Flue Gas
100°C
Hg
Knockout
SOx and NOx
removal
VSEP
H2O
MgCl2.2H2O
Flue Gas 440°C
MgCl2 (conc) recycle

FIG. 16

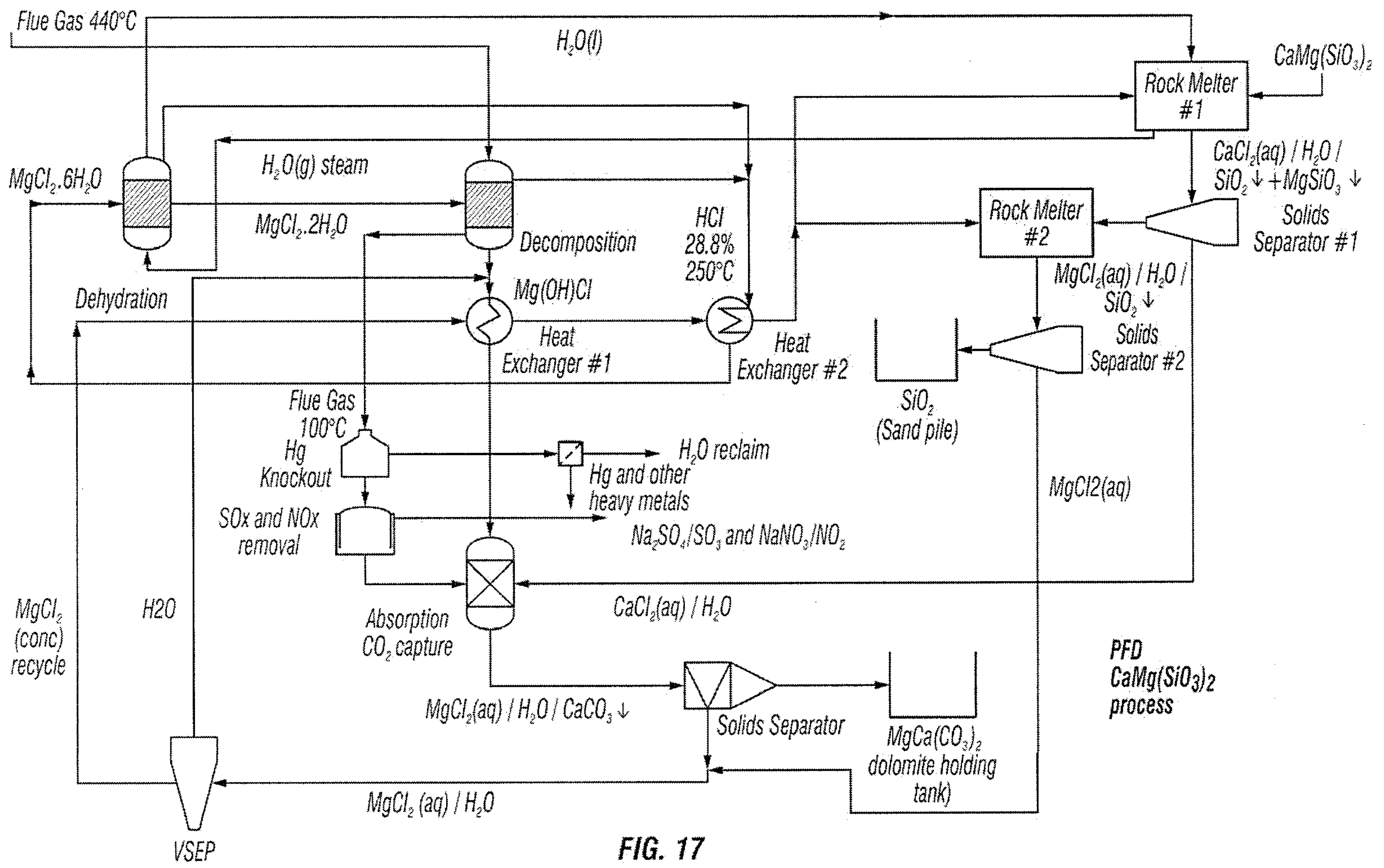
Flue Gas 440°C
$H_2O(l)$
Rock Melter #1
$CaMg(SiO_3)_2$
$MgCl_2.6H_2O$
$H_2O(g)$ steam
$MgCl_2.2H_2O$
Decomposition
HCl 28.8% 250°C
$CaCl_2(aq) / H_2O / SiO_2\downarrow + MgSiO_3\downarrow$
Rock Melter #2
Solids Separator #1
Dehydration
$Mg(OH)Cl$
$MgCl_2(aq) / H_2O / SiO_2\downarrow$
Heat Exchanger #1
Heat Exchanger #2
Solids Separator #2
SiO_2 (Sand pile)
Flue Gas 100°C
Hg Knockout
H_2O reclaim
Hg and other heavy metals
MgCl2(aq)
SOx and NOx removal
Na_2SO_4/SO_3 and $NaNO_3/NO_2$
$MgCl_2$ (conc) recycle
H2O
Absorption CO_2 capture
$CaCl_2(aq) / H_2O$
PFD $CaMg(SiO_3)_2$ process
$MgCl_2(aq) / H_2O / CaCO_3\downarrow$
Solids Separator
$MgCa(CO_3)_2$ dolomite holding tank)
$MgCl_2$ (aq) / H_2O
VSEP

FIG. 17

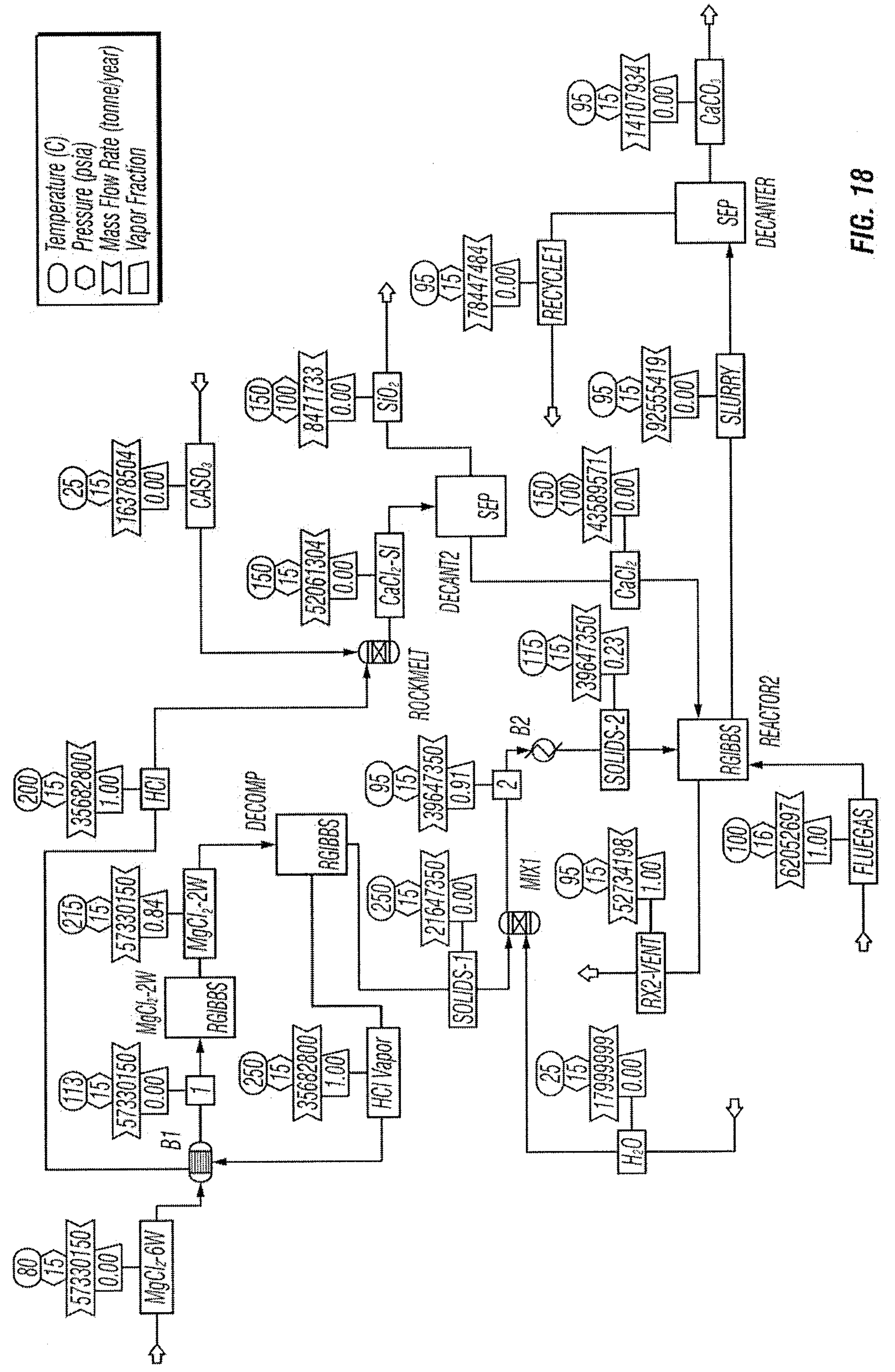
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Vapor Fraction
MgCl₂-6W
80
15
57330150
0.00
B1
1
113
15
57330150
0.00
MgCl₂-2W
RGIBBS
MgCl₂-2W
215
15
57330150
0.84
DECOMP
RGIBBS
HCl Vapor
250
15
35682800
1.00
HCl
200
15
35682800
1.00
SOLIDS-1
250
15
21647350
0.00
MIX1
H₂O
25
15
17999999
0.00
2
95
15
39647350
0.91
B2
SOLIDS-2
115
15
39647350
0.23
RX2-VENT
95
15
52734198
1.00
FLUEGAS
100
16
62052697
1.00
REACTOR2
RGIBBS
ROCKMELT
CASO₃
25
15
16378504
0.00
CaCl₂-SI
150
15
52061304
0.00
DECANT2
SEP
SiO₂
150
100
8471733
0.00
CaCl₂
150
100
43589571
0.00
SLURRY
95
15
92555419
0.00
RECYCLE1
95
15
78447484
0.00
DECANTER
SEP
CaCO₃
95
15
14107934
0.00

FIG. 18

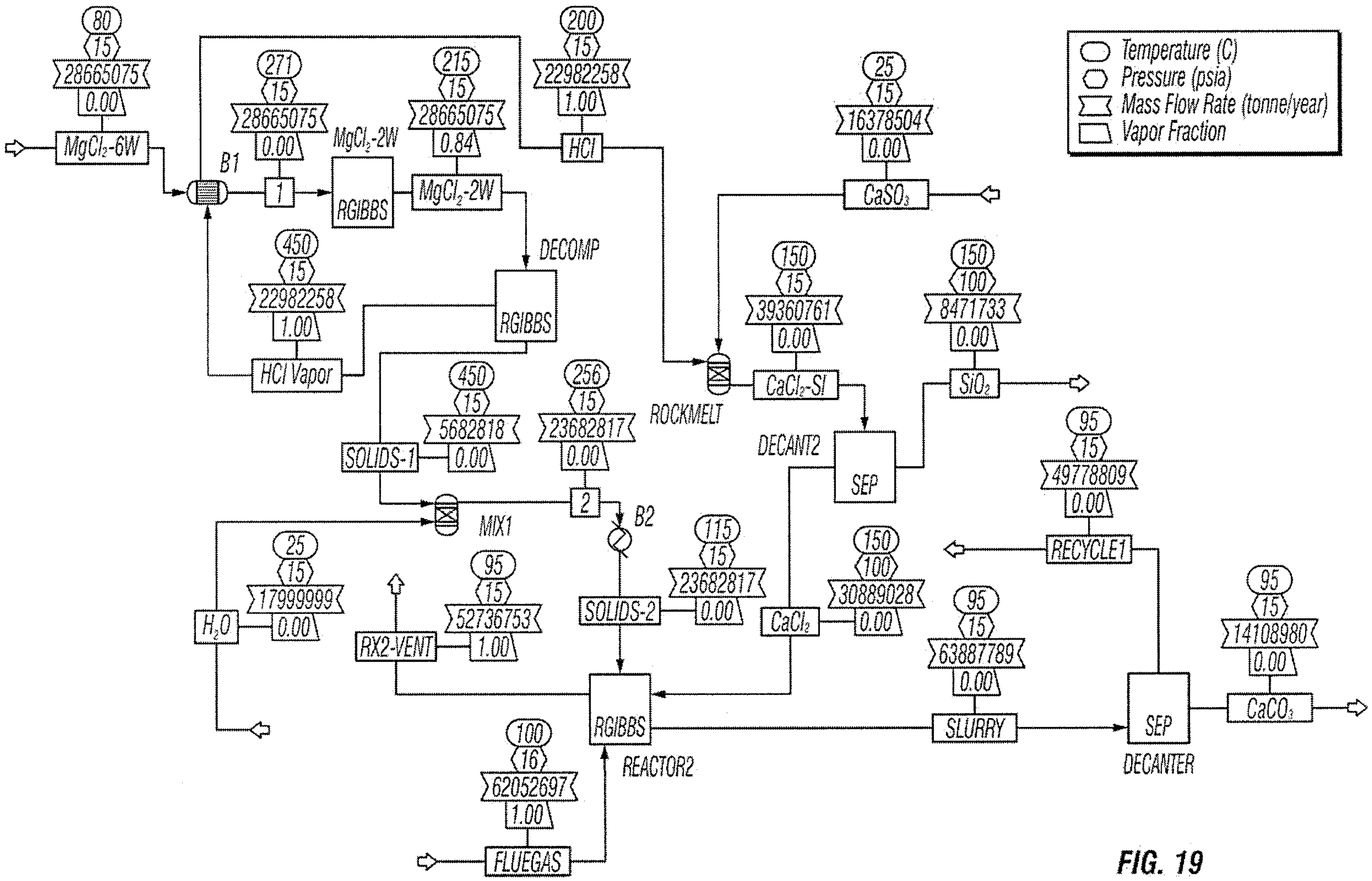
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Vapor Fraction
80
15
28665075
0.00
MgCl₂-6W
B1
271
15
28665075
0.00
1
MgCl₂-2W
RGIBBS
215
15
28665075
0.84
MgCl₂-2W
200
15
22982258
1.00
HCl
DECOMP
RGIBBS
450
15
22982258
1.00
HCl Vapor
25
15
16378504
0.00
CaSO₃
150
15
39360761
0.00
CaCl₂-SI
ROCKMELT
150
100
8471733
0.00
SiO₂
DECANT2
SEP
450
15
5682818
0.00
SOLIDS-1
256
15
23682817
0.00
2
B2
MIX1
25
15
17999999
0.00
H₂O
95
15
52736753
1.00
RX2-VENT
115
15
23682817
0.00
SOLIDS-2
150
100
30889028
0.00
CaCl₂
95
15
49778809
0.00
RECYCLE1
RGIBBS
REACTOR2
95
15
63887789
0.00
SLURRY
SEP
DECANTER
95
15
14108980
0.00
CaCO₃
100
16
62052697
1.00
FLUEGAS

FIG. 19

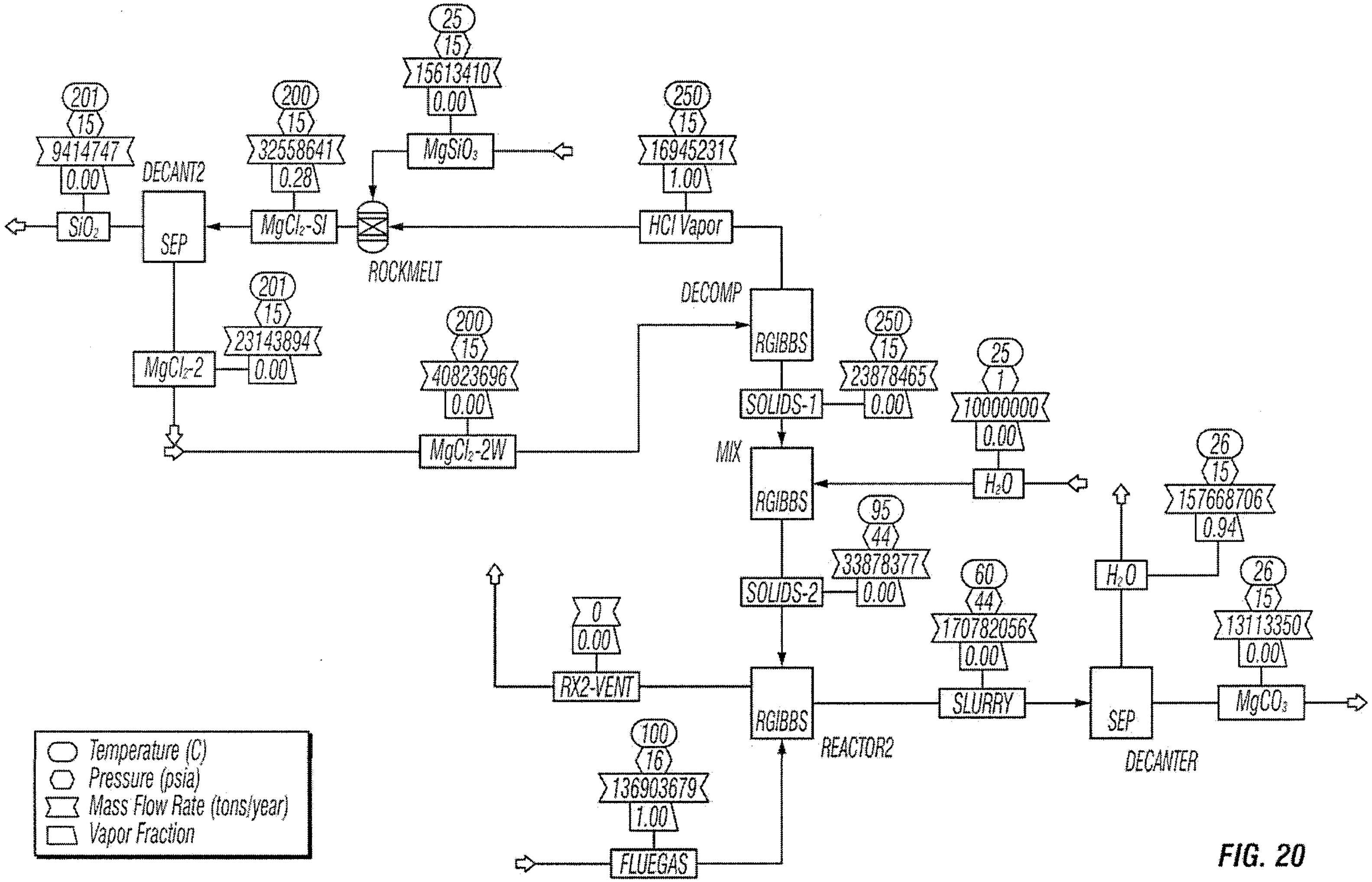
201
15
9414747
0.00
SiO₂
DECANT2
SEP
200
15
32558641
0.28
MgCl₂-SI
25
15
15613410
0.00
MgSiO₃
ROCKMELT
250
15
16945231
1.00
HCl Vapor
201
15
23143894
0.00
MgCl₂-2
200
15
40823696
0.00
MgCl₂-2W
DECOMP
RGIBBS
250
15
23878465
0.00
SOLIDS-1
25
1
10000000
0.00
H₂O
MIX
RGIBBS
95
44
33878377
0.00
SOLIDS-2
0
0.00
RX2-VENT
RGIBBS
REACTOR2
100
16
136903679
1.00
FLUEGAS
60
44
170782056
0.00
SLURRY
26
15
157668706
0.94
H₂O
SEP
DECANTER
26
15
13113350
0.00
MgCO₃
Temperature (C)
Pressure (psia)
Mass Flow Rate (tons/year)
Vapor Fraction

FIG. 20

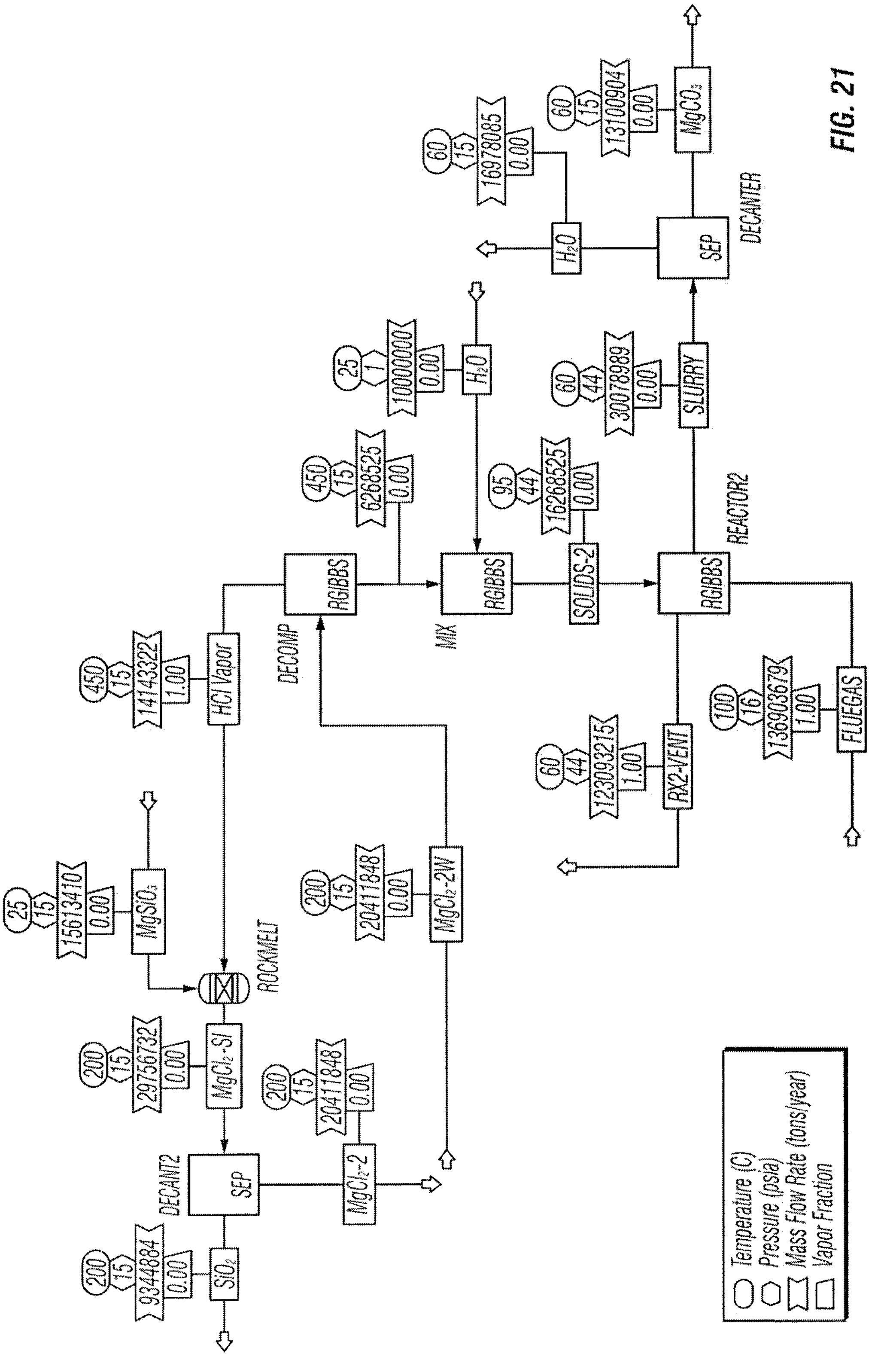
25
15
15613410
0.00
$MgSiO_3$
ROCKMELT
450
15
14143322
1.00
HCl Vapor
200
15
29756732
0.00
$MgCl_2$-SI
DECANT2
SEP
200
15
9344884
0.00
SiO_2
200
15
20411848
0.00
$MgCl_2$-2
200
15
20411848
0.00
$MgCl_2$-2W
DECOMP
RGIBBS
450
15
6268525
0.00
MIX
RGIBBS
25
1
10000000
0.00
H_2O
95
44
16268525
0.00
SOLIDS-2
REACTOR2
RGIBBS
60
44
123093215
1.00
RX2-VENT
100
16
136903679
1.00
FLUEGAS
60
44
30078989
0.00
SLURRY
DECANTER
SEP
60
15
16978085
0.00
H_2O
60
15
13100904
0.00
$MgCO_3$
Temperature (C)
Pressure (psia)
Mass Flow Rate (tons/year)
Vapor Fraction

FIG. 21

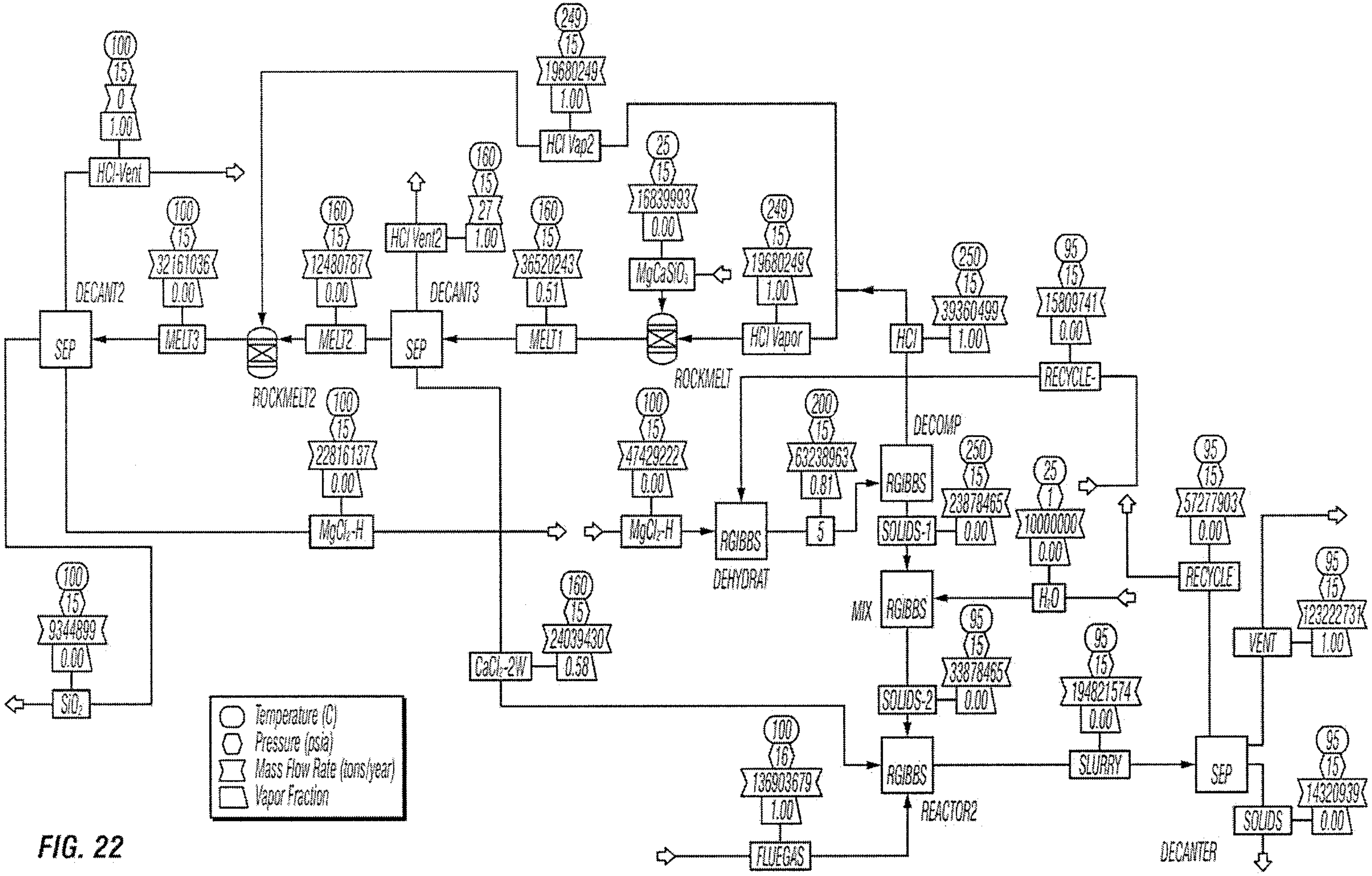
100
15
0
1.00
HCl-Vent
249
15
19680249
1.00
HCl Vap2
160
15
27
1.00
HCl Vent2
25
15
16839993
0.00
MgCaSiO$_3$
249
15
19680249
1.00
HCl Vapor
250
15
39360499
1.00
HCl
95
15
15809741
0.00
RECYCLE-
100
15
32161036
0.00
MELT3
160
15
12480787
0.00
MELT2
160
15
36520243
0.51
MELT1
DECANT2
SEP
ROCKMELT2
DECANT3
SEP
ROCKMELT
100
15
22816137
0.00
MgCl$_2$-H
100
15
47429222
0.00
MgCl$_2$-H
RGIBBS
DEHYDRAT
200
15
63238963
0.81
5
DECOMP
RGIBBS
250
15
23878465
0.00
SOLIDS-1
25
1
10000000
0.00
H$_2$O
MIX
RGIBBS
95
15
33878465
0.00
SOLIDS-2
95
15
57277903
0.00
RECYCLE
95
15
12322273
1.00
VENT
100
15
9344899
0.00
SiO$_2$
160
15
24039430
0.58
CaCl$_2$-2W
100
16
136903679
1.00
FLUEGAS
RGIBBS
REACTOR2
95
15
194821574
0.00
SLURRY
SEP
DECANTER
95
15
14320939
0.00
SOLIDS
Temperature (C)
Pressure (psia)
Mass Flow Rate (tons/year)
Vapor Fraction

FIG. 22

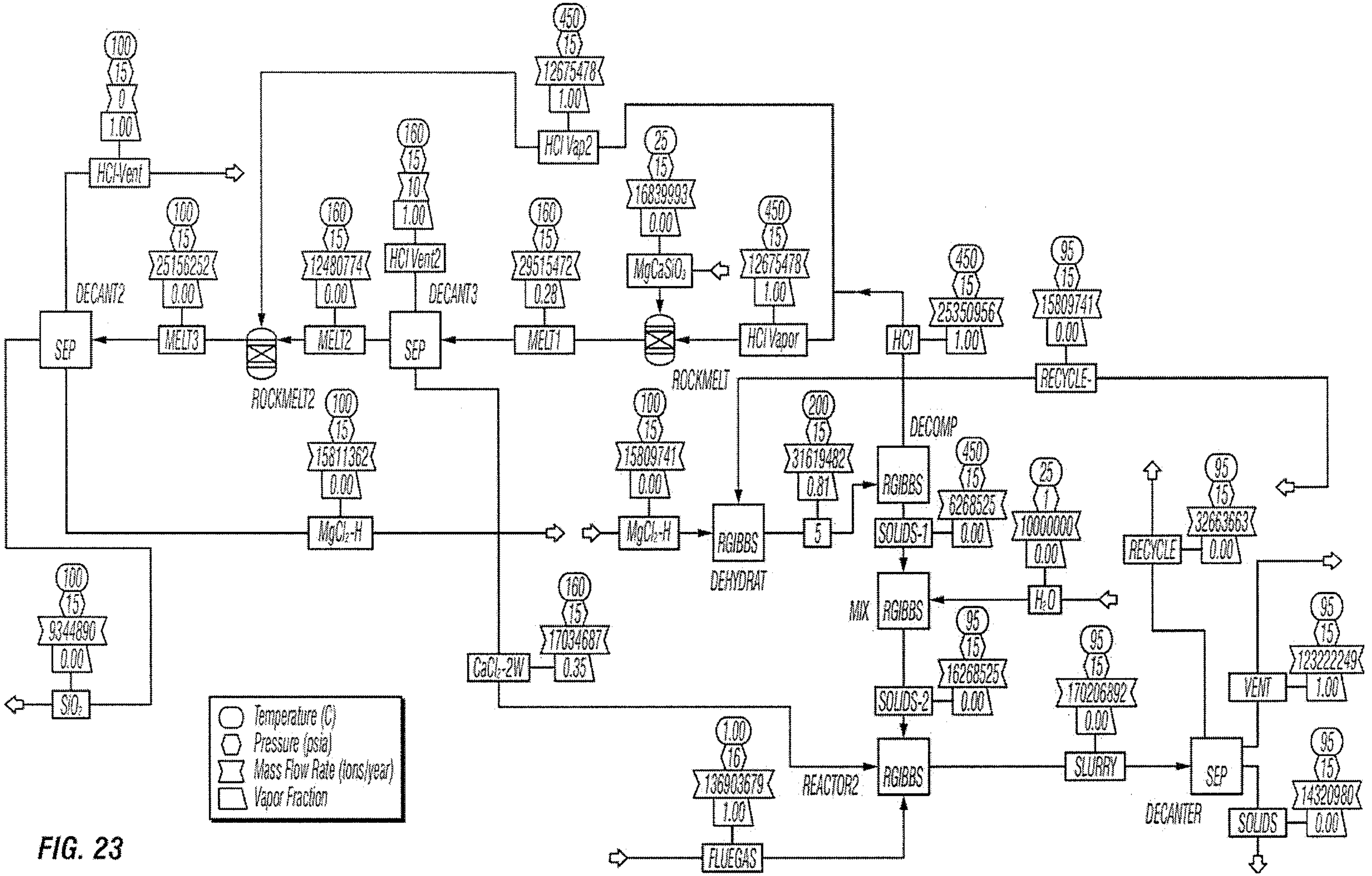
100
15
0
1.00
HCl-Vent
450
15
12675478
1.00
HCl Vap2
160
15
10
1.00
HCl Vent2
25
15
16839993
0.00
MgCaSiO₃
450
15
12675478
1.00
HCl Vapor
450
15
25350956
1.00
HCl
95
15
15809741
0.00
RECYCLE-
DECANT2
SEP
100
15
25156252
0.00
MELT3
ROCKMELT2
160
15
12480774
0.00
MELT2
DECANT3
SEP
160
15
29515472
0.28
MELT1
ROCKMELT
100
15
15811362
0.00
MgCl₂-H
100
15
15809741
0.00
MgCl₂-H
RGIBBS
DEHYDRAT
200
15
31619482
0.81
5
DECOMP
RGIBBS
450
15
6268525
0.00
SOLIDS-1
25
1
10000000
0.00
H₂O
MIX
RGIBBS
95
15
16268525
0.00
SOLIDS-2
160
15
17034687
0.35
CaCl₂-2W
100
15
9344890
0.00
SiO₂
Temperature (C)
Pressure (psia)
Mass Flow Rate (tons/year)
Vapor Fraction
1.00
16
136903679
1.00
FLUEGAS
REACTOR2
RGIBBS
95
15
170206892
0.00
SLURRY
95
15
32663663
0.00
RECYCLE
SEP
DECANTER
95
15
123222249
1.00
VENT
95
15
14320980
0.00
SOLIDS

FIG. 23

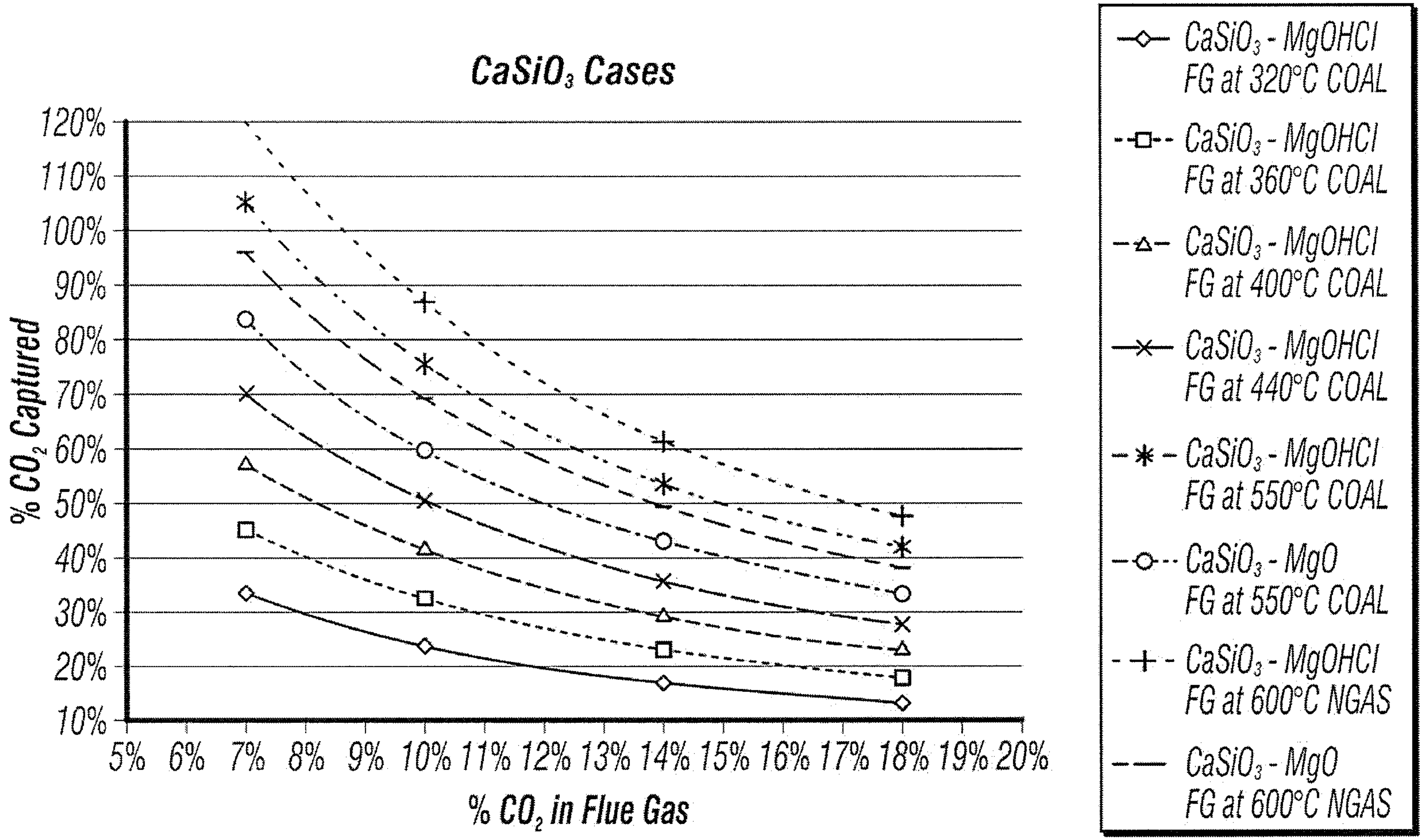
CaSiO₃ Cases
% CO₂ Captured
120%
110%
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
5%
6%
7%
8%
9%
10%
11%
12%
13%
14%
15%
16%
17%
18%
19%
20%
% CO₂ in Flue Gas
CaSiO₃ - MgOHCl FG at 320°C COAL
CaSiO₃ - MgOHCl FG at 360°C COAL
CaSiO₃ - MgOHCl FG at 400°C COAL
CaSiO₃ - MgOHCl FG at 440°C COAL
CaSiO₃ - MgOHCl FG at 550°C COAL
CaSiO₃ - MgO FG at 550°C COAL
CaSiO₃ - MgOHCl FG at 600°C NGAS
CaSiO₃ - MgO FG at 600°C NGAS

FIG. 24

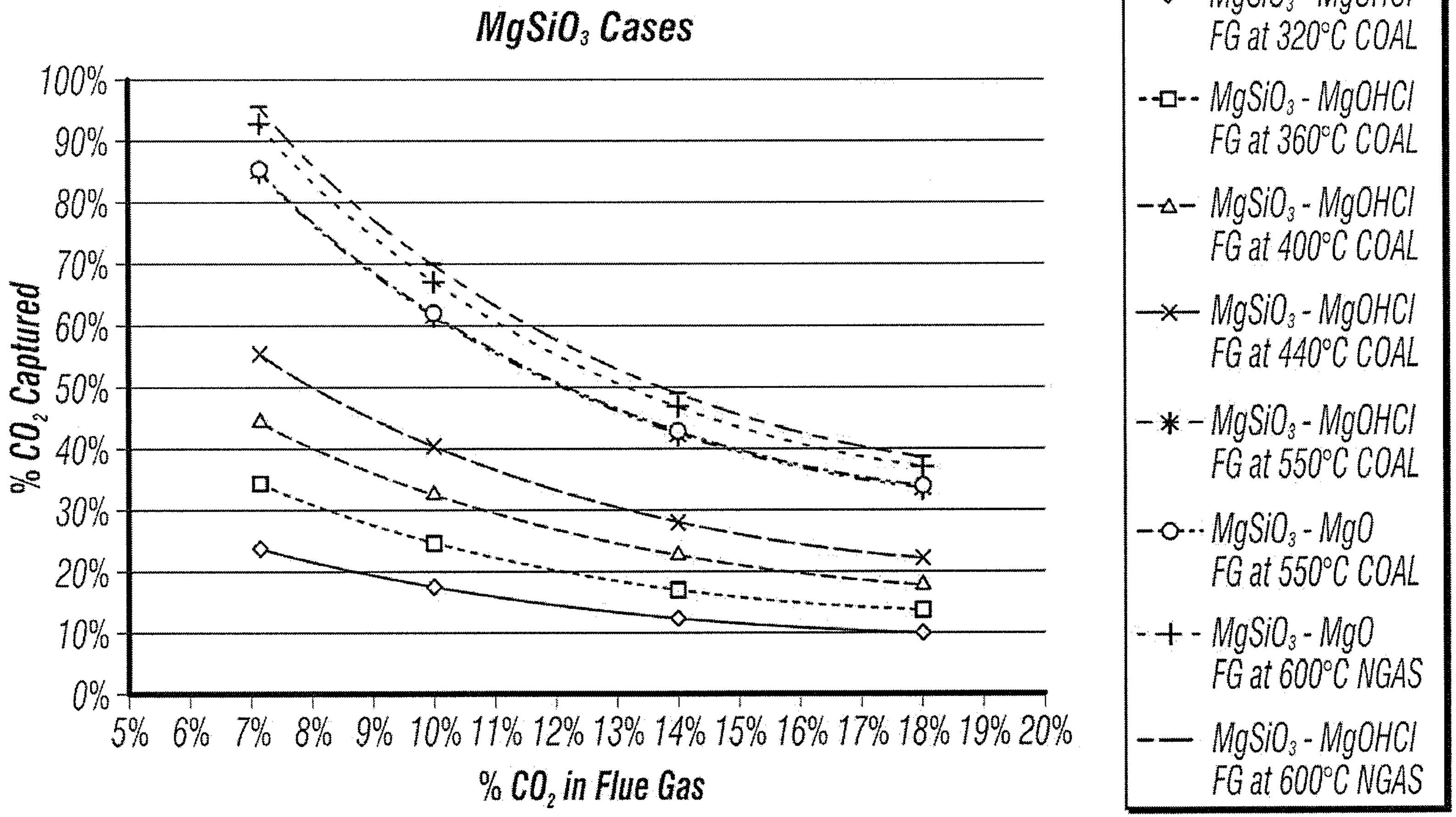
MgSiO$_3$ Cases
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% CO$_2$ Captured
5%
6%
7%
8%
9%
10%
11%
12%
13%
14%
15%
16%
17%
18%
19%
20%
% CO$_2$ in Flue Gas
MgSiO$_3$ - MgOHCl FG at 320°C COAL
MgSiO$_3$ - MgOHCl FG at 360°C COAL
MgSiO$_3$ - MgOHCl FG at 400°C COAL
MgSiO$_3$ - MgOHCl FG at 440°C COAL
MgSiO$_3$ - MgOHCl FG at 550°C COAL
MgSiO$_3$ - MgO FG at 550°C COAL
MgSiO$_3$ - MgO FG at 600°C NGAS
MgSiO$_3$ - MgOHCl FG at 600°C NGAS

FIG. 25

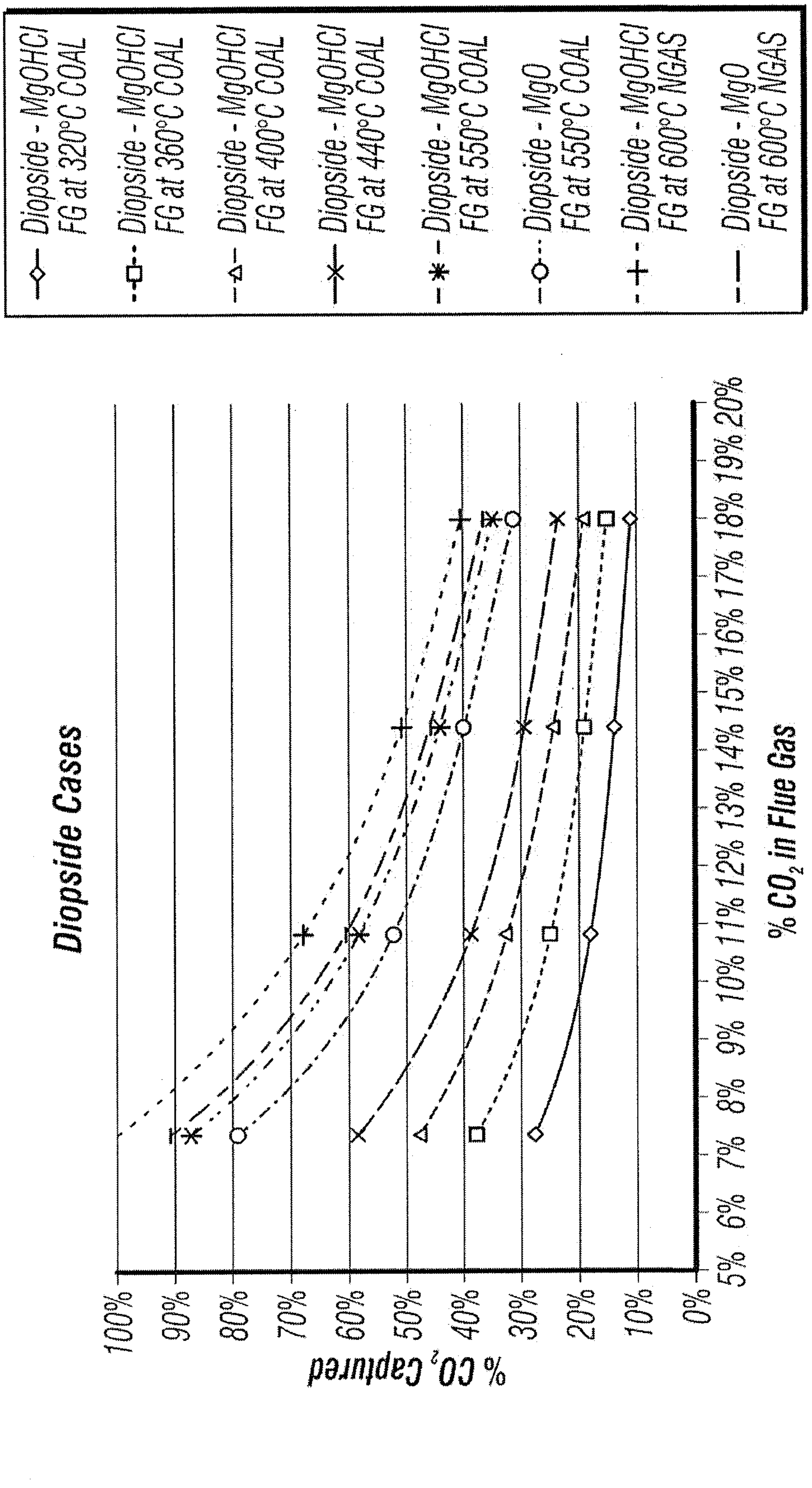
Diopside Cases
% CO$_2$ Captured
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5%
6%
7%
8%
9%
10%
11%
12%
13%
14%
15%
16%
17%
18%
19%
20%
% CO$_2$ in Flue Gas
Diopside - MgOHCl FG at 320°C COAL
Diopside - MgOHCl FG at 360°C COAL
Diopside - MgOHCl FG at 400°C COAL
Diopside - MgOHCl FG at 440°C COAL
Diopside - MgOHCl FG at 550°C COAL
Diopside - MgO FG at 550°C COAL
Diopside - MgOHCl FG at 600°C NGAS
Diopside - MgO FG at 600°C NGAS

FIG. 26

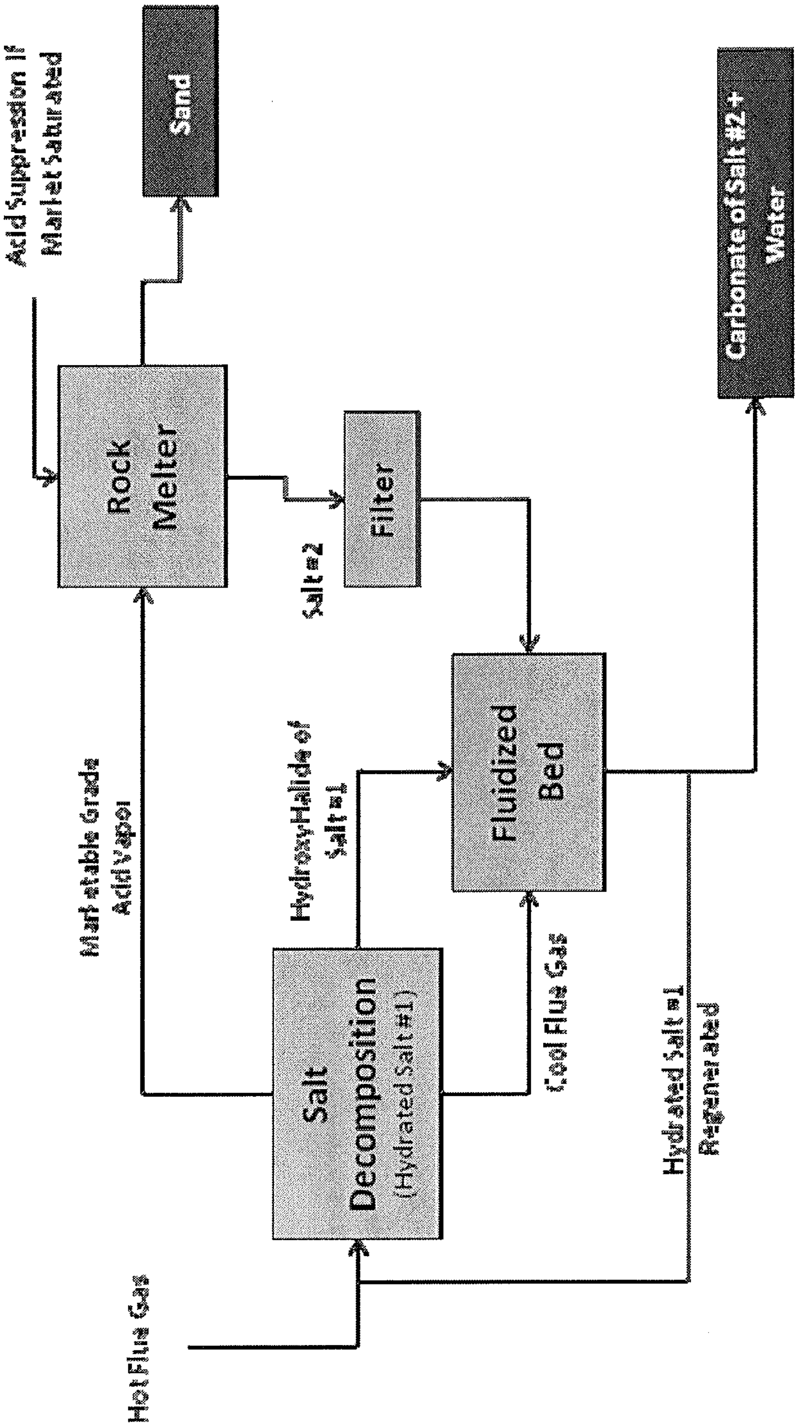
Hot Flue Gas
Salt Decomposition (Hydrated Salt #1)
Marketable Grade Acid Vapor
Acid Suppression If Market Saturated
Rock Melter
Sand
Salt #2
Filter
HydroxyHalide of Salt #1
Cool Flue Gas
Fluidized Bed
Hydrated Salt #1 Regenerated
Carbonate of Salt #2 + Water

FIG. 27

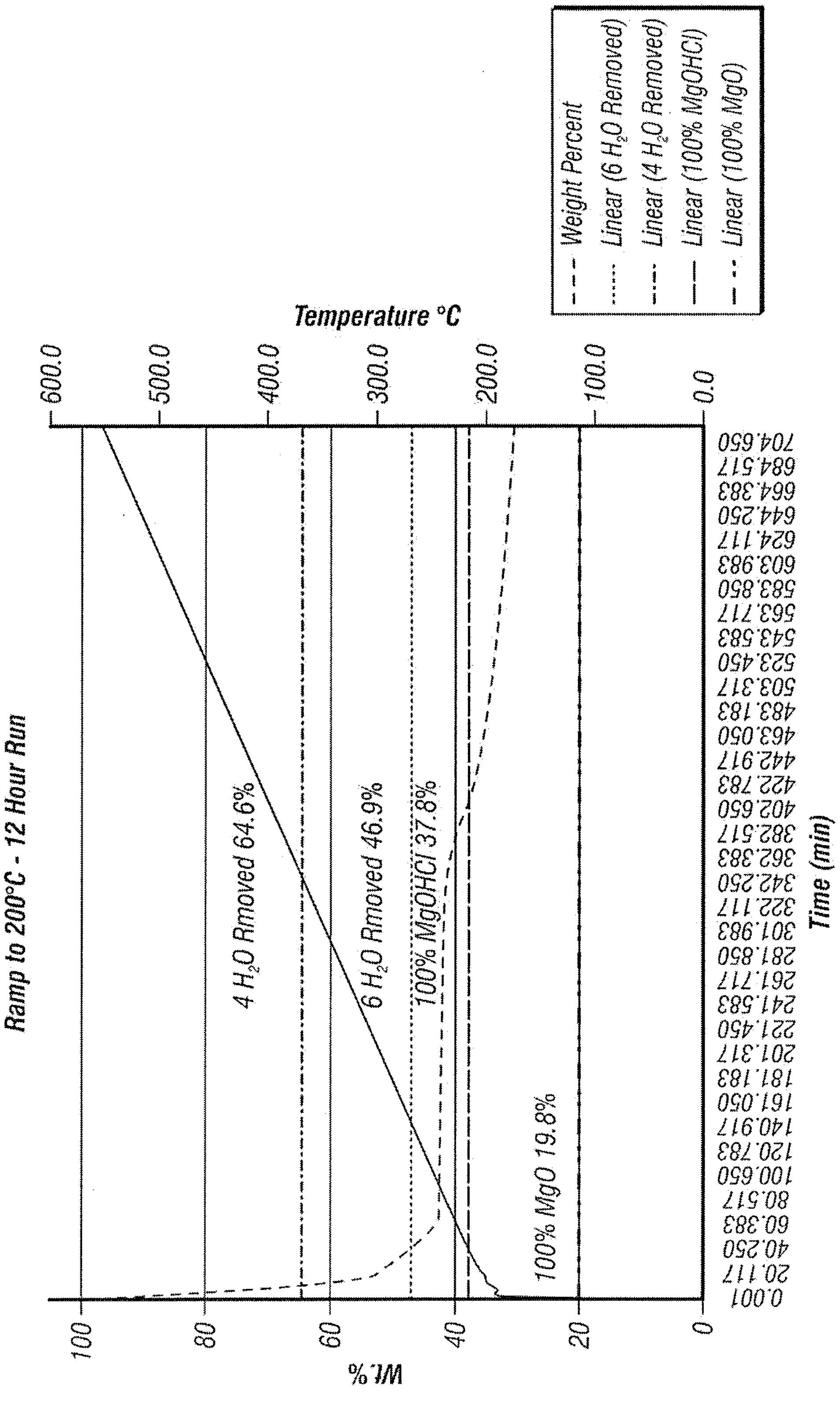
Ramp to 200°C - 12 Hour Run
Temperature °C
600.0
500.0
400.0
300.0
200.0
100.0
0.0
Wt.%
100
80
60
40
20
0
Time (min)
0.001
20.117
40.250
60.383
80.517
100.650
120.783
140.917
161.050
181.183
201.317
221.450
241.583
261.717
281.850
301.983
322.117
342.250
362.383
382.517
402.650
422.783
442.917
463.050
483.183
503.317
523.450
543.583
563.717
583.850
603.983
624.117
644.250
664.383
684.517
704.650
4 H_2O Rmoved 64.6%
6 H_2O Rmoved 46.9%
100% MgOHCl 37.8%
100% MgO 19.8%
Weight Percent
Linear (6 H_2O Removed)
Linear (4 H_2O Removed)
Linear (100% MgOHCl)
Linear (100% MgO)

FIG. 28

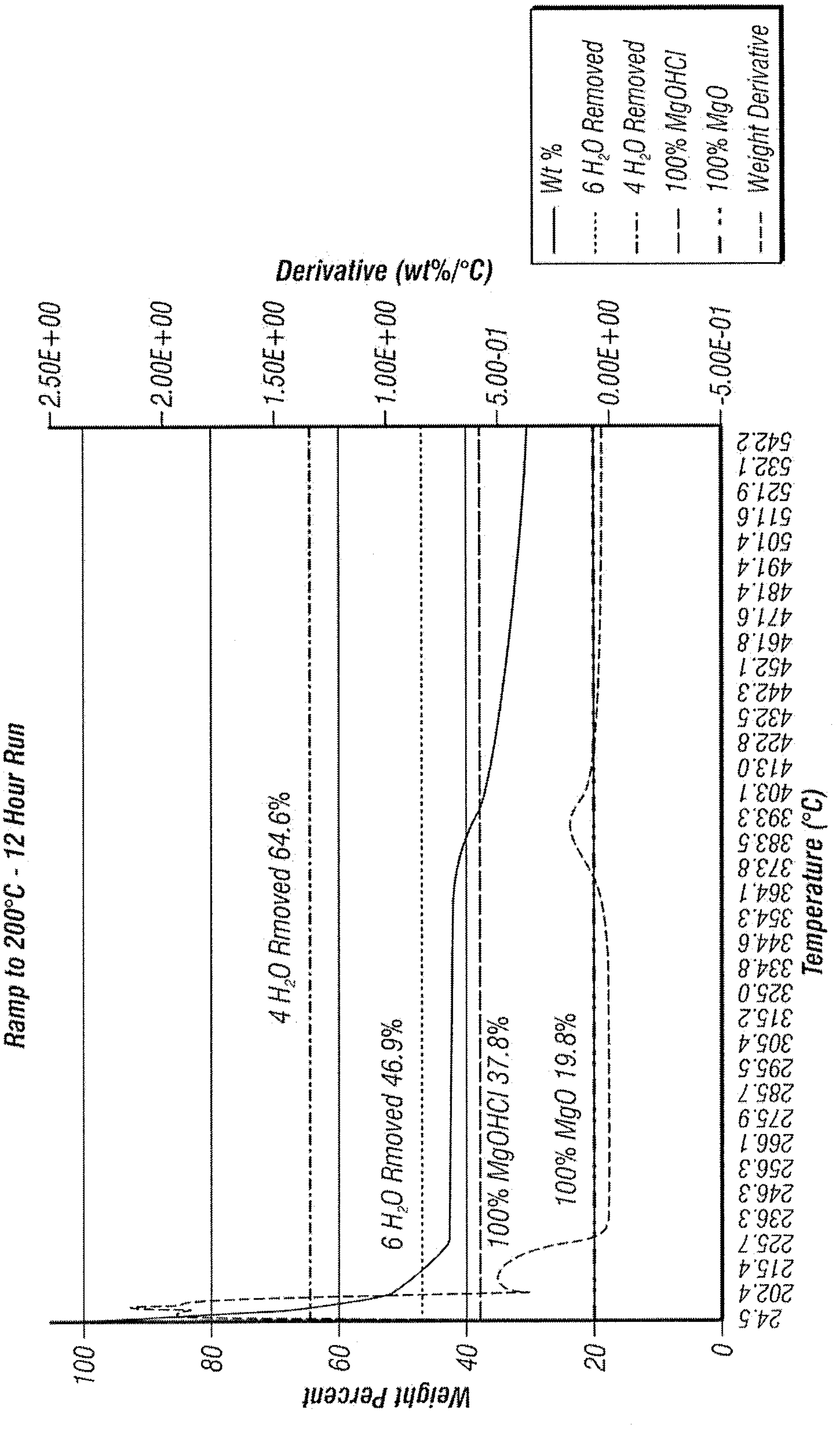
Ramp to 200°C - 12 Hour Run
Derivative (wt%/°C)
2.50E+00
2.00E+00
1.50E+00
1.00E+00
5.00-01
0.00E+00
-5.00E-01
Weight Percent
100
80
60
40
20
0
Temperature (°C)
24.5
202.4
215.4
225.7
236.3
246.3
256.3
266.1
275.9
285.7
295.5
305.4
315.2
325.0
334.8
344.6
354.3
364.1
373.8
383.5
393.3
403.1
413.0
422.8
432.5
442.3
452.1
461.8
471.6
481.4
491.4
501.4
511.6
521.9
532.1
542.2
4 H_2O Rmoved 64.6%
6 H_2O Rmoved 46.9%
100% MgOHCl 37.8%
100% MgO 19.8%
Wt %
6 H_2O Removed
4 H_2O Removed
100% MgOHCl
100% MgO
Weight Derivative

FIG. 29

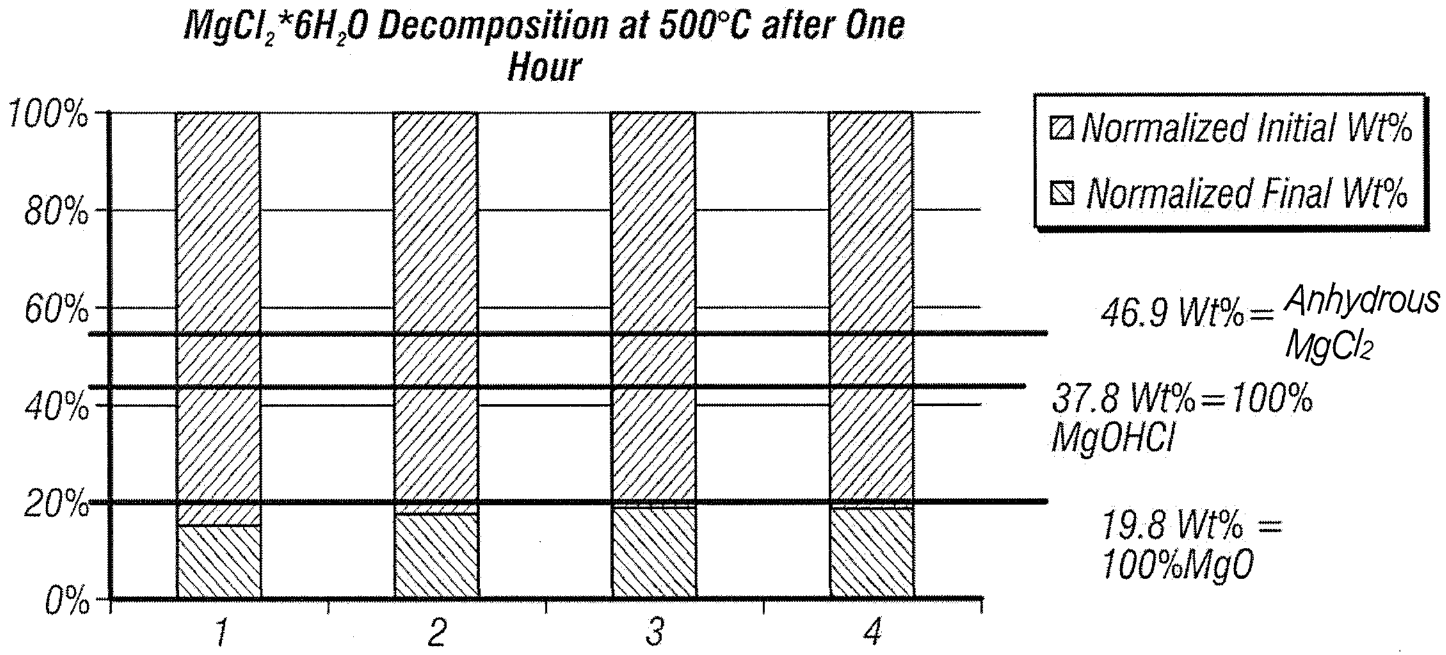
MgCl₂*6H₂O Decomposition at 500°C after One Hour
100%
80%
60%
40%
20%
0%
1
2
3
4
▨ Normalized Initial Wt%
▧ Normalized Final Wt%
46.9 Wt%= Anhydrous MgCl2
37.8 Wt%=100% MgOHCl
19.8 Wt% = 100%MgO

FIG. 30

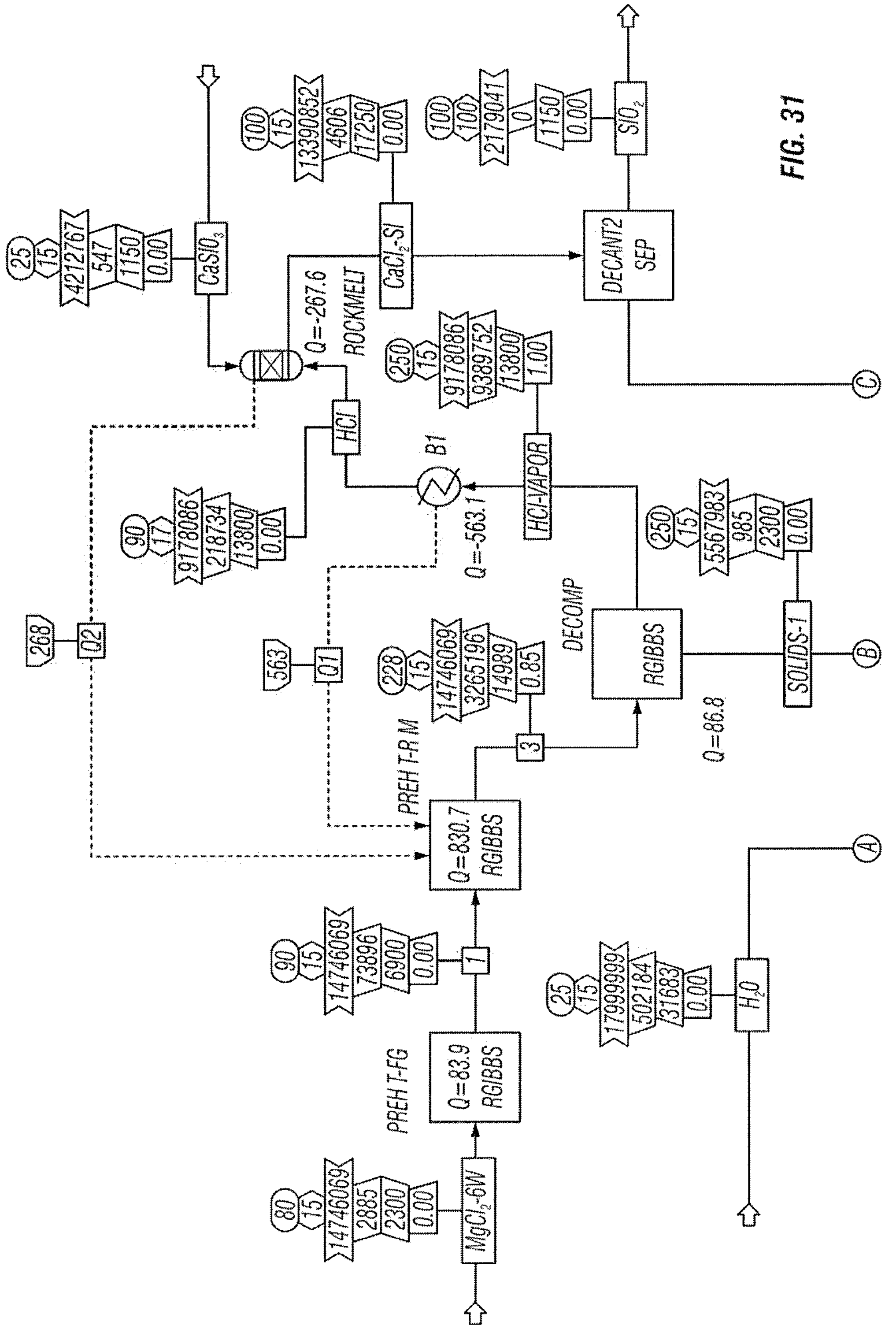
MgCl$_2$-6W
80
15
14746069
2885
2300
0.00
PREH T-FG
Q=83.9
RGIBBS
1
90
15
14746069
73896
6900
0.00
PREH T-R M
Q=830.7
RGIBBS
3
228
15
14746069
3265196
14989
0.85
DECOMP
RGIBBS
Q=86.8
SOLIDS-1
250
15
5567983
985
2300
0.00
B
HCl-VAPOR
250
15
9178086
9389752
13800
1.00
B1
Q=-563.1
HCl
90
17
9178086
218734
13800
0.00
Q1
563
Q2
268
ROCKMELT
Q=-267.6
CaSiO$_3$
25
15
4212767
547
1150
0.00
CaCl$_2$-SI
100
15
13390852
4606
17250
0.00
DECANT2
SEP
SIO$_2$
100
100
2179041
0
1150
0.00
C
H$_2$O
25
15
17999999
502184
31683
0.00
A

FIG. 31

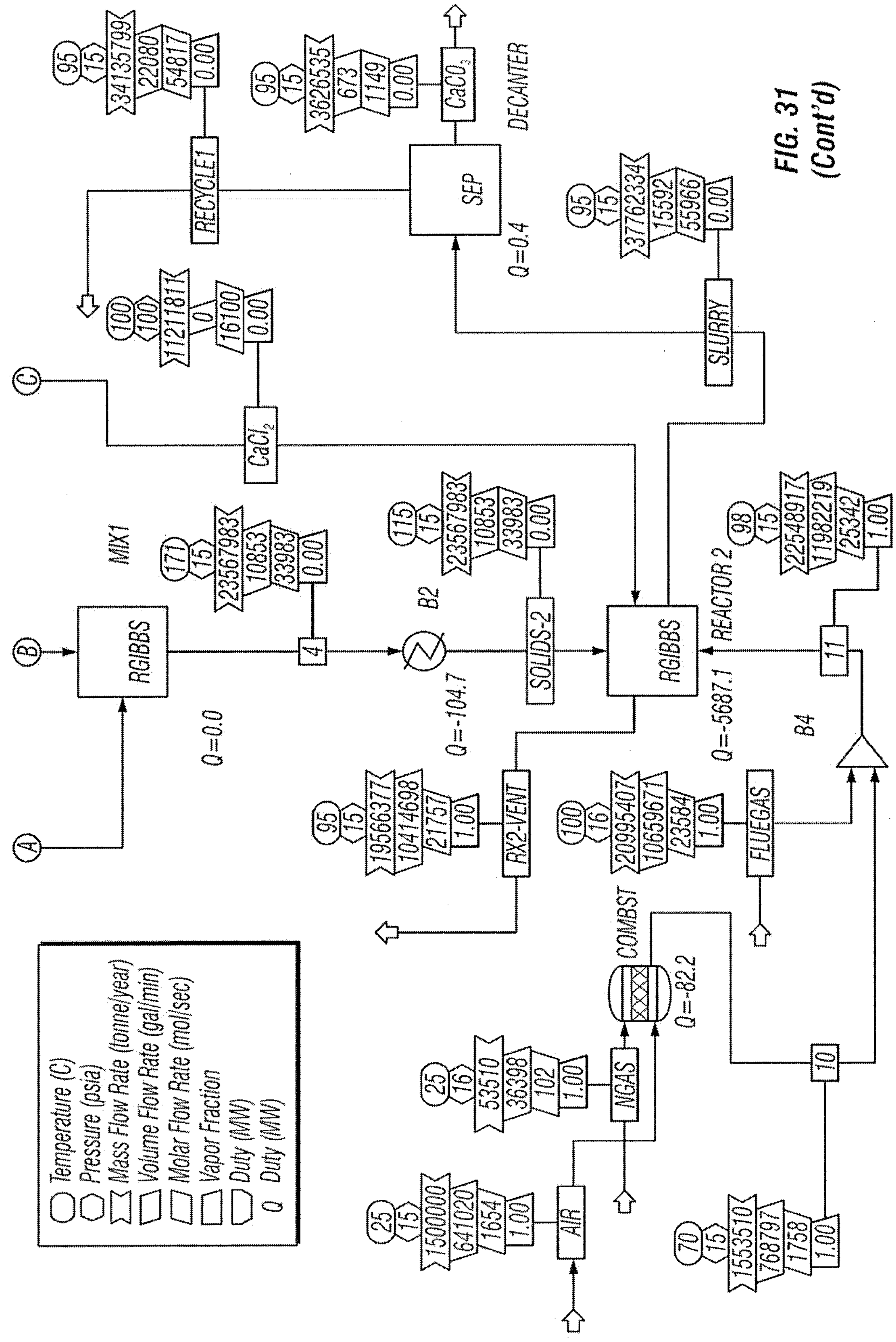
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)
A
B
C
RGIBBS
MIX1
Q=0.0
4
171
15
23567983
10853
33983
0.00
B2
Q=-104.7
115
15
23567983
10853
33983
0.00
SOLIDS-2
RGIBBS
REACTOR 2
Q=-5687.1
CaCl2
100
100
1121181
0
16100
0.00
RECYCLE1
95
15
34135799
22080
54817
0.00
SEP
Q=0.4
CaCO3
DECANTER
95
15
3626535
673
1149
0.00
SLURRY
95
15
37762334
15592
55966
0.00
11
98
15
22548917
11982219
25342
1.00
B4
RX2-VENT
95
15
19566377
10414698
21757
1.00
FLUEGAS
100
16
20995407
10659671
23584
1.00
COMBST
Q=-82.2
NGAS
25
16
53510
36398
102
1.00
AIR
25
15
1500000
641020
1654
1.00
10
70
15
1553510
768797
1758
1.00

FIG. 31 (Cont'd)

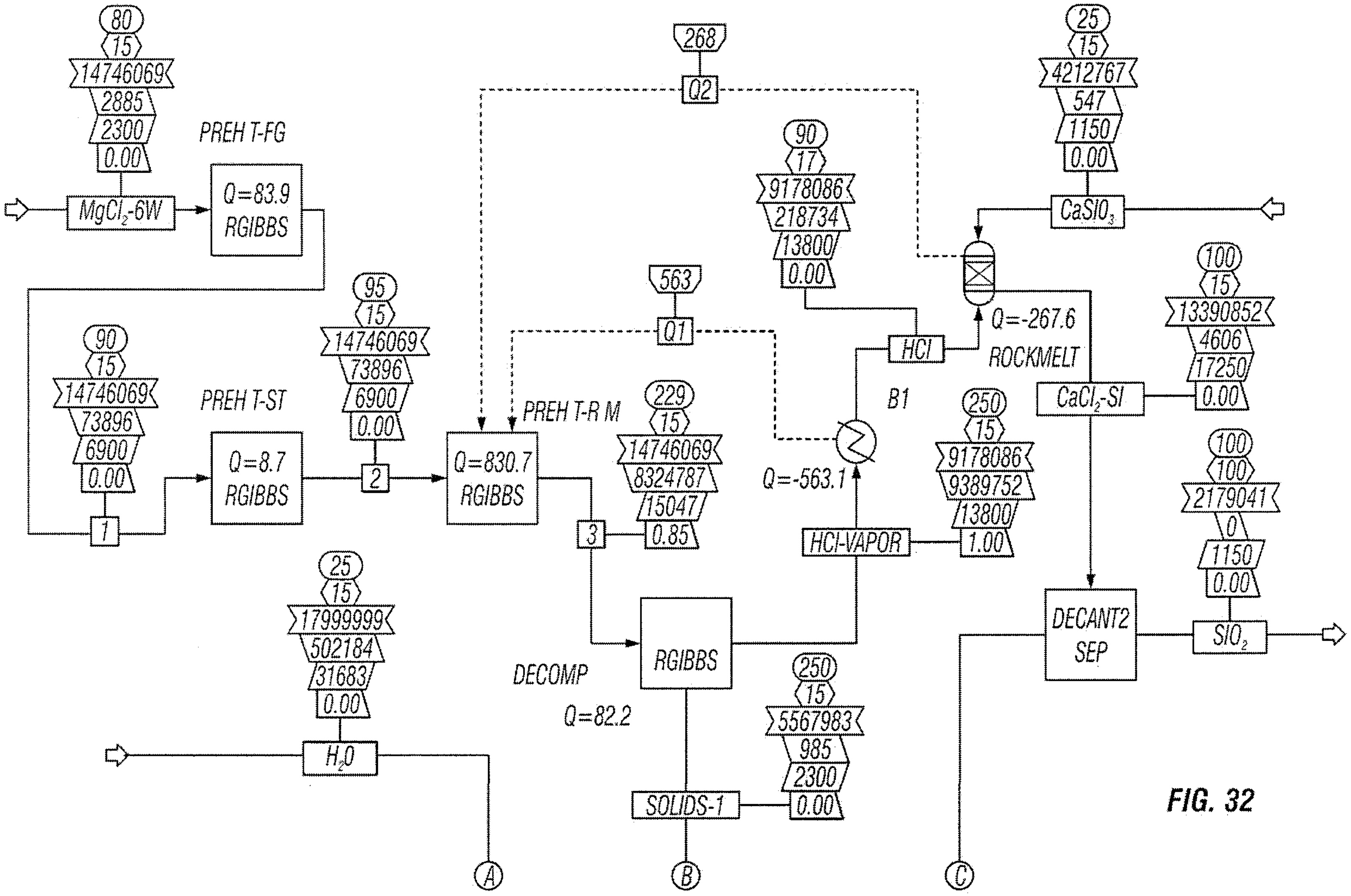
80
15
14746069
2885
2300
0.00
$MgCl_2$-6W
PREH T-FG
Q=83.9
RGIBBS
90
15
14746069
73896
6900
0.00
1
PREH T-ST
Q=8.7
RGIBBS
95
15
14746069
73896
6900
0.00
2
268
Q2
563
Q1
PREH T-R M
Q=830.7
RGIBBS
229
15
14746069
8324787
15047
0.85
3
25
15
17999999
502184
31683
0.00
H_2O
A
DECOMP
Q=82.2
RGIBBS
250
15
5567983
985
2300
0.00
SOLIDS-1
B
90
17
9178086
218734
13800
0.00
HCl
B1
Q=-563.1
250
15
9178086
9389752
13800
1.00
HCl-VAPOR
25
15
4212767
547
1150
0.00
$CaSiO_3$
Q=-267.6
ROCKMELT
100
15
13390852
4606
17250
0.00
$CaCl_2$-SI
DECANT2
SEP
100
100
2179041
0
1150
0.00
SiO_2
C

FIG. 32

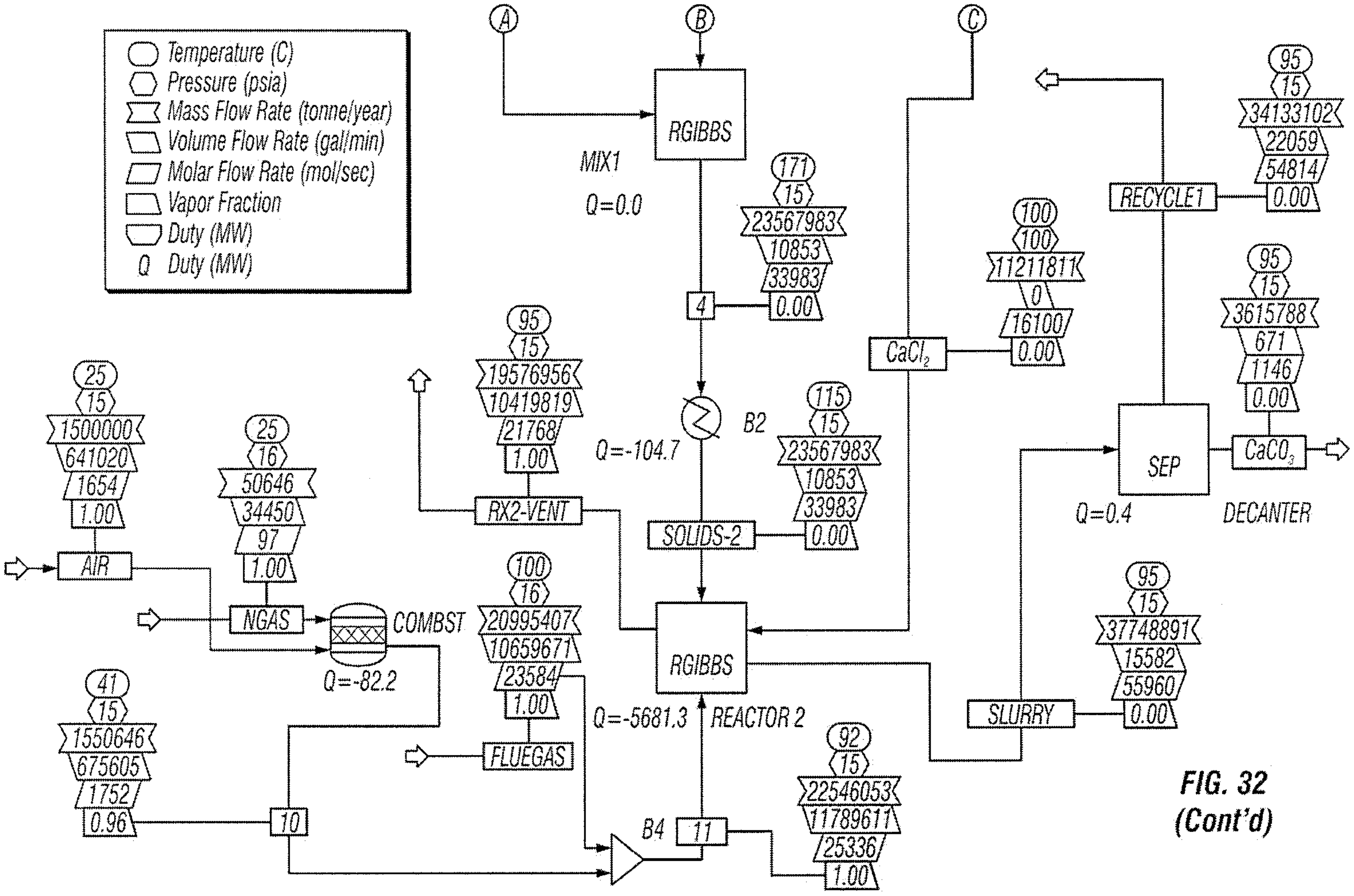
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)
A
B
C
RGIBBS
MIX1
Q=0.0
171
15
23567983
10853
33983
0.00
4
B2
Q=-104.7
115
15
23567983
10853
33983
0.00
SOLIDS-2
95
15
19576956
10419819
21768
1.00
RX2-VENT
CaCl$_2$
100
100
11211811
0
16100
0.00
RGIBBS
REACTOR 2
Q=-5681.3
SLURRY
95
15
37748891
15582
55960
0.00
SEP
Q=0.4
DECANTER
CaCO$_3$
95
15
3615788
671
1146
0.00
RECYCLE1
95
15
34133102
22059
54814
0.00
25
15
1500000
641020
1654
1.00
AIR
25
16
50646
34450
97
1.00
NGAS
COMBST
Q=-82.2
100
16
20995407
10659671
23584
1.00
FLUEGAS
41
15
1550646
675605
1752
0.96
10
B4
11
92
15
22546053
11789611
25336
1.00

FIG. 32
(Cont'd)

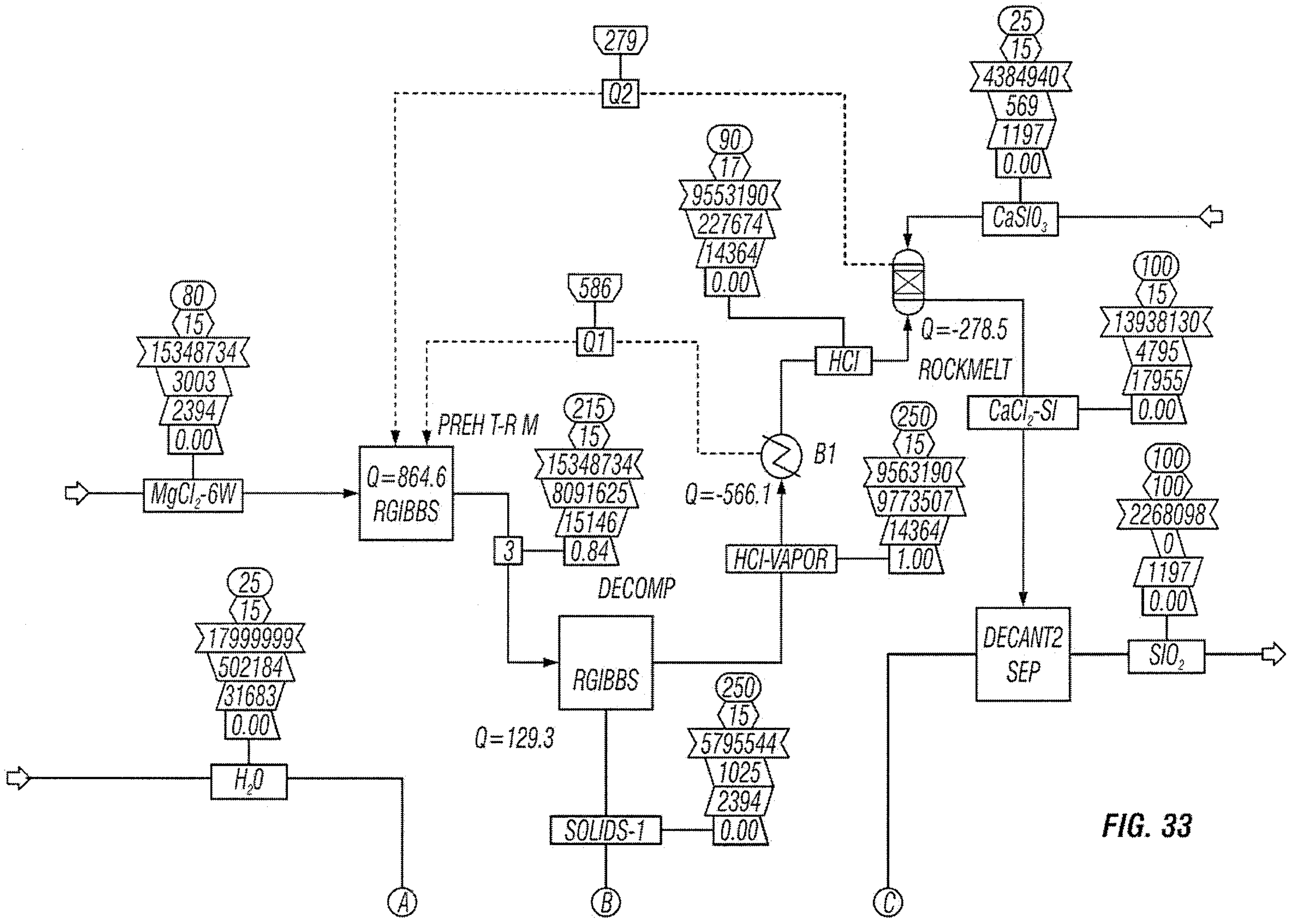
279
Q2
25
15
4384940
569
1197
0.00
$CaSiO_3$
90
17
9553190
227674
14364
0.00
586
Q1
80
15
15348734
3003
2394
0.00
$MgCl_2$-6W
Q=864.6
RGIBBS
PREH T-R M
215
15
15348734
8091625
15146
0.84
3
HCl
Q=-278.5
ROCKMELT
100
15
13938130
4795
17955
0.00
$CaCl_2$-SI
B1
Q=-566.1
250
15
9563190
9773507
14364
1.00
HCl-VAPOR
DECOMP
RGIBBS
Q=129.3
100
100
2268098
0
1197
0.00
DECANT2
SEP
SiO_2
25
15
17999999
502184
31683
0.00
H_2O
250
15
5795544
1025
2394
0.00
SOLIDS-1
A
B
C

FIG. 33

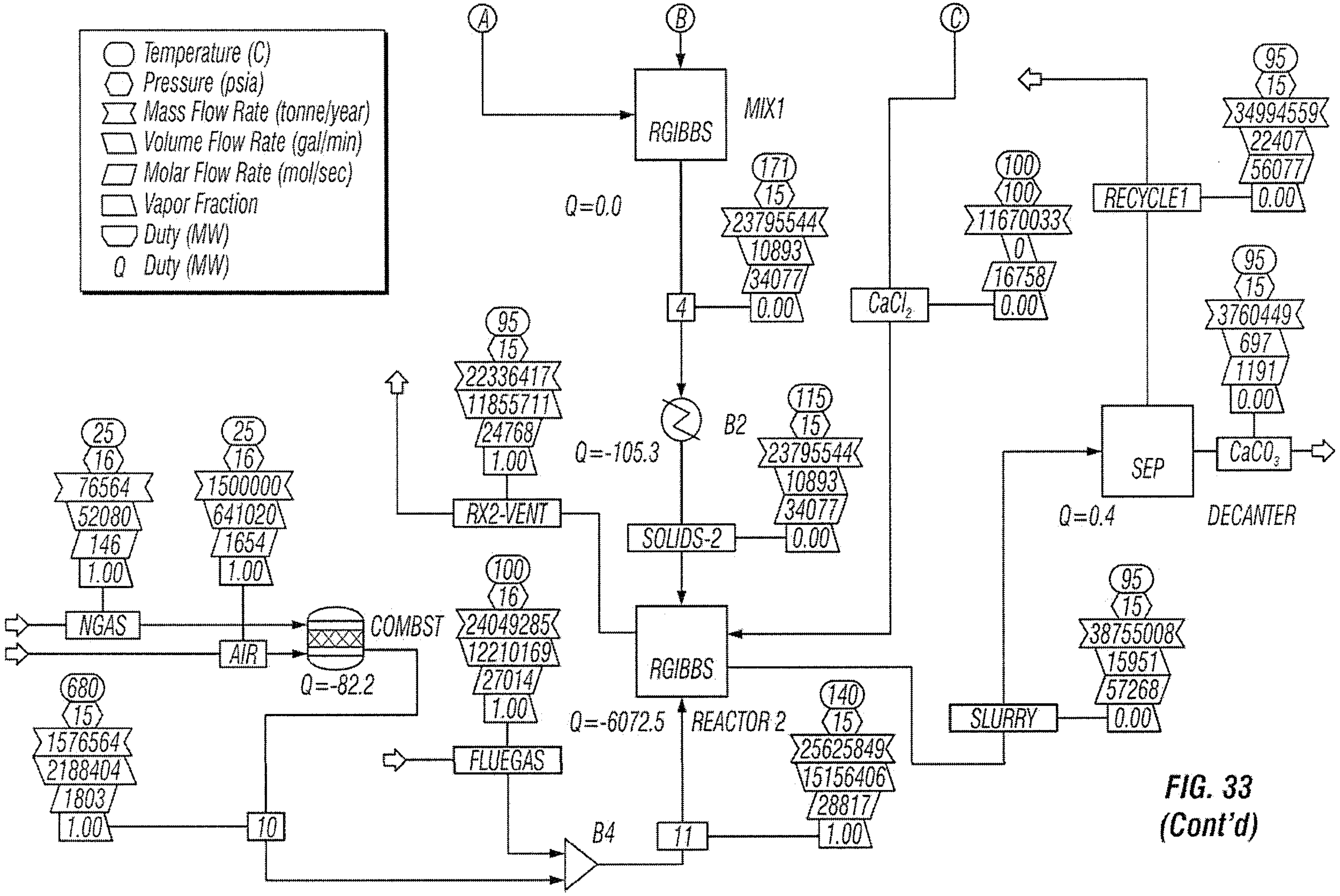
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)
A
B
C
RGIBBS
MIX1
Q=0.0
171
15
23795544
10893
34077
0.00
4
B2
Q=-105.3
115
15
23795544
10893
34077
0.00
SOLIDS-2
CaCl$_2$
100
100
11670033
0
16758
0.00
RECYCLE1
95
15
34994559
22407
56077
0.00
SEP
Q=0.4
DECANTER
CaCO$_3$
95
15
3760449
697
1191
0.00
95
15
22336417
11855711
24768
1.00
RX2-VENT
RGIBBS
REACTOR 2
Q=-6072.5
SLURRY
95
15
38755008
15951
57268
0.00
25
16
76564
52080
146
1.00
NGAS
25
16
1500000
641020
1654
1.00
AIR
COMBST
Q=-82.2
100
16
24049285
12210169
27014
1.00
FLUEGAS
680
15
1576564
2188404
1803
1.00
10
B4
11
140
15
25625849
15156406
28817
1.00

FIG. 33
(Cont'd)

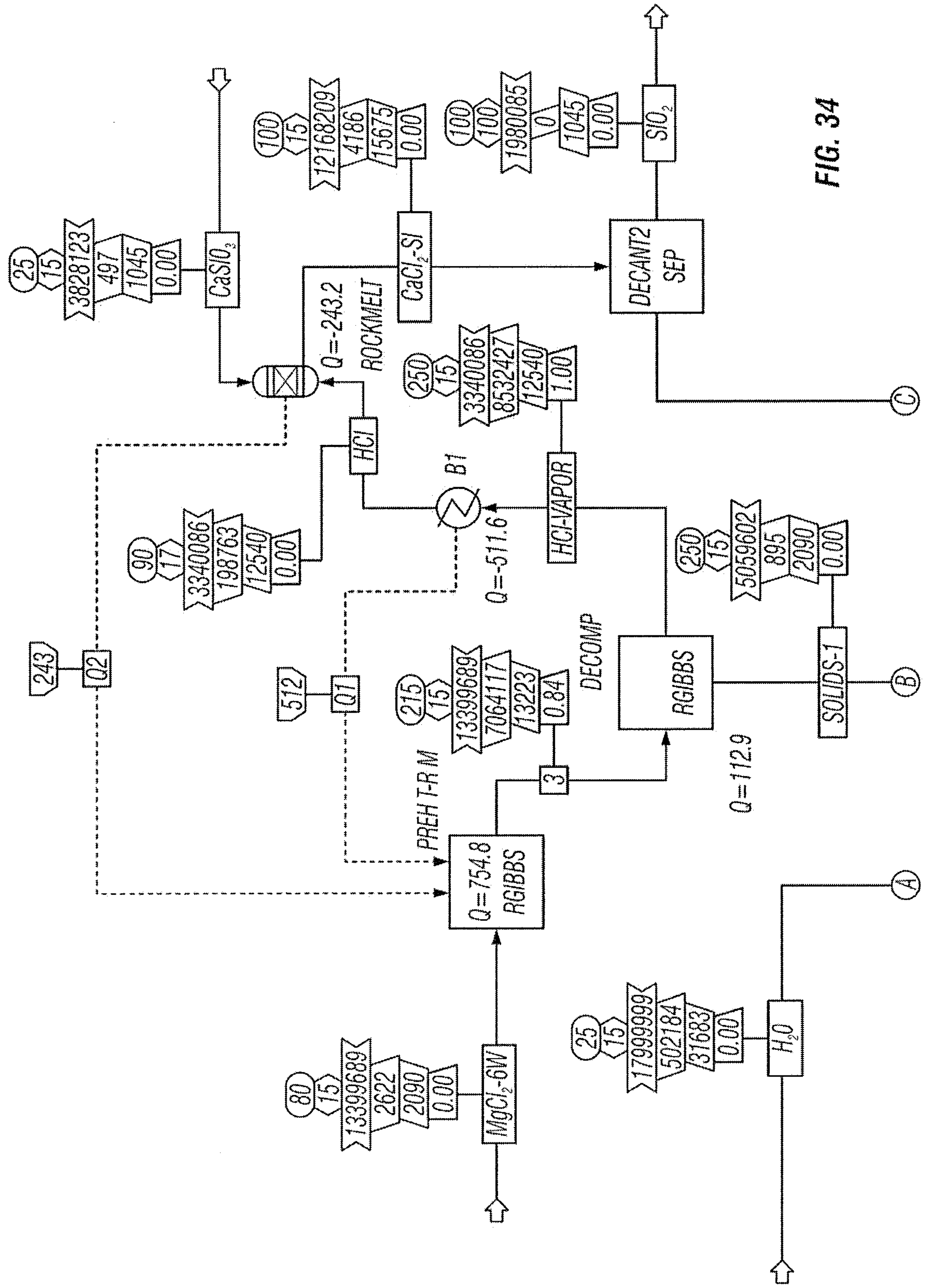
MgCl$_2$-6W
80
15
13399689
2622
2090
0.00
Q=754.8
RGIBBS
PREH T-R M
3
215
15
13399689
7064117
13223
0.84
RGIBBS
DECOMP
Q=112.9
Q1
512
Q2
243
B1
Q=-511.6
HCl-VAPOR
250
15
3340086
8532427
12540
1.00
HCl
90
17
3340086
198763
12540
0.00
ROCKMELT
Q=-243.2
CaSiO$_3$
25
15
3828123
497
1045
0.00
CaCl$_2$-SI
100
15
12168209
4186
15675
0.00
DECANT2
SEP
SiO$_2$
100
100
1980085
0
1045
0.00
SOLIDS-1
250
15
5059602
895
2090
0.00
H$_2$O
25
15
17999999
502184
31683
0.00
A
B
C

FIG. 34

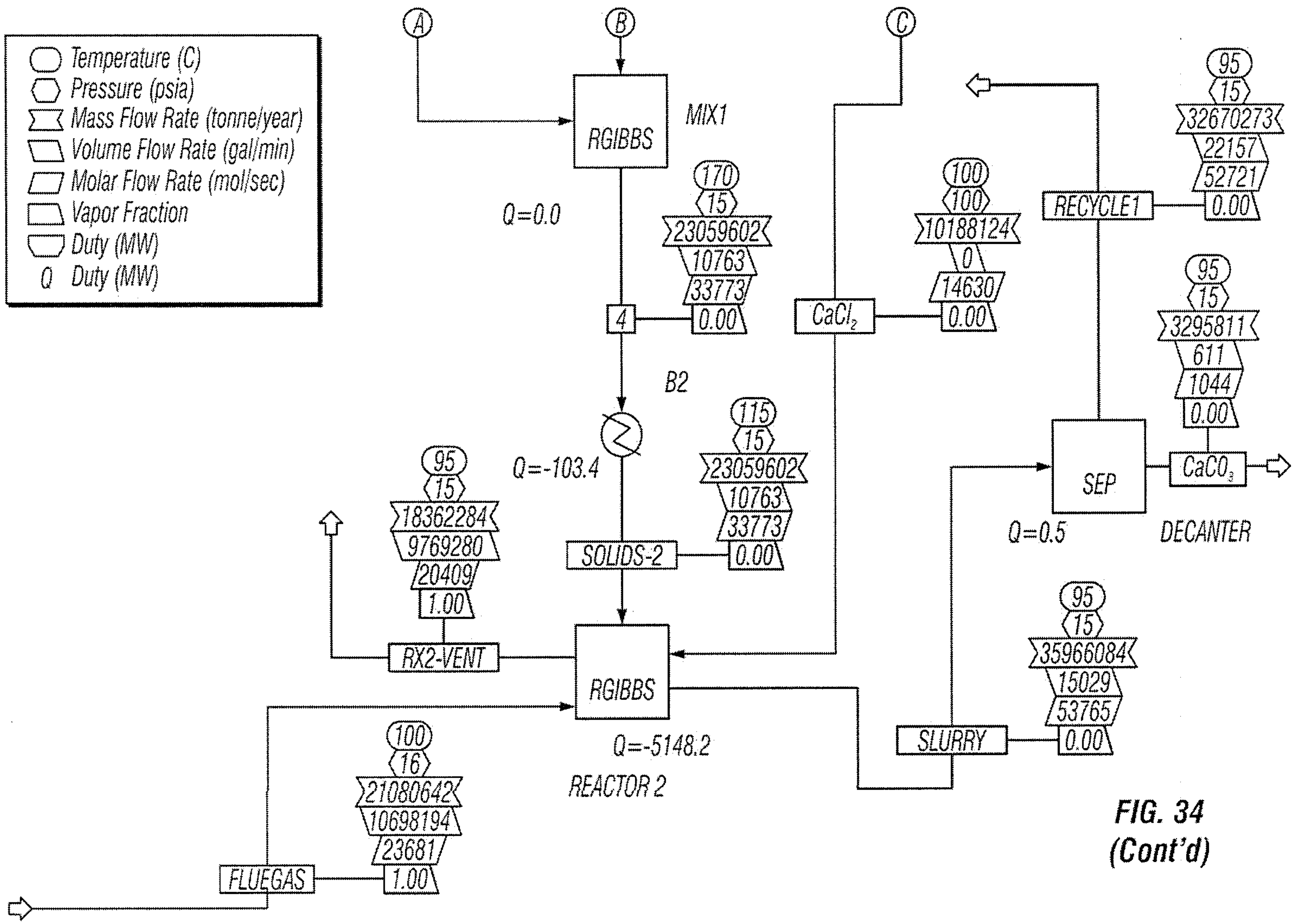
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)
A
B
C
RGIBBS
MIX1
Q=0.0
170
15
23059602
10763
33773
0.00
4
B2
Q=-103.4
115
15
23059602
10763
33773
0.00
SOLIDS-2
CaCl$_2$
100
100
10188124
0
14630
0.00
RGIBBS
Q=-5148.2
REACTOR 2
95
15
18362284
9769280
20409
1.00
RX2-VENT
100
16
21080642
10698194
23681
1.00
FLUEGAS
SLURRY
95
15
35966084
15029
53765
0.00
SEP
Q=0.5
DECANTER
CaCO$_3$
95
15
3295811
611
1044
0.00
RECYCLE1
95
15
32670273
22157
52721
0.00

FIG. 34
(Cont'd)

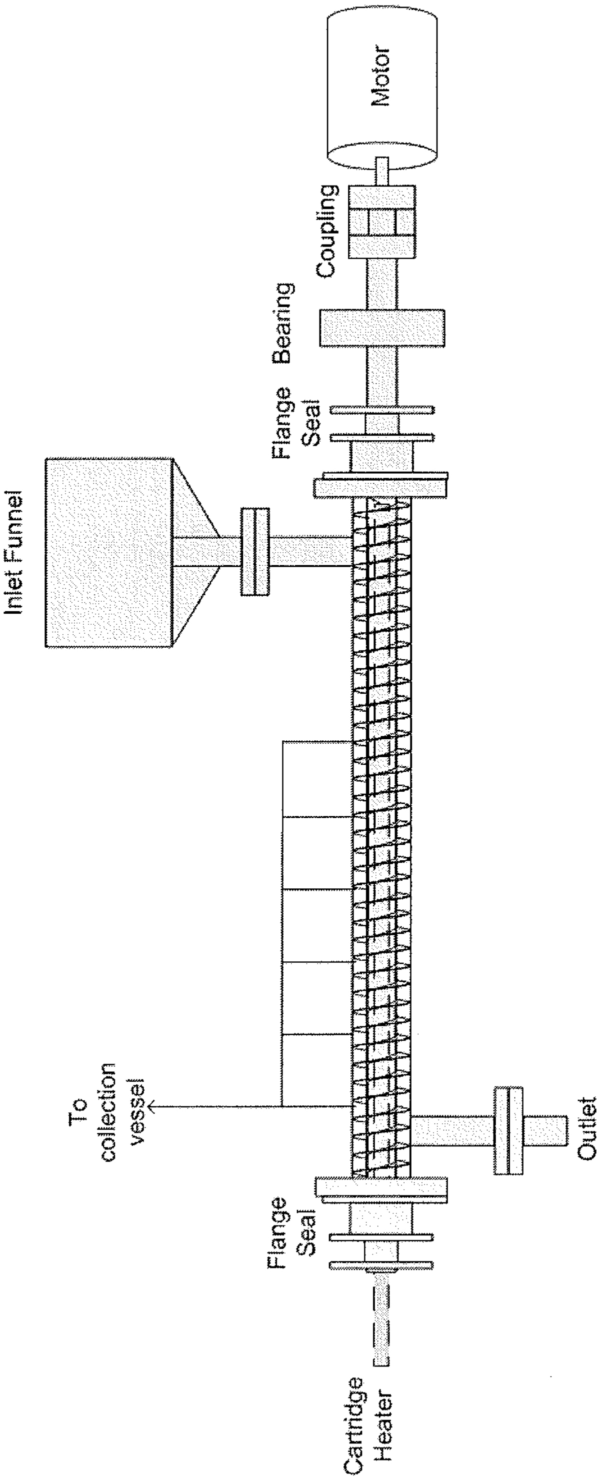
Motor
Coupling
Bearing
Flange Seal
Inlet Funnel
To collection vessel
Outlet
Flange Seal
Cartridge Heater

FIG. 35

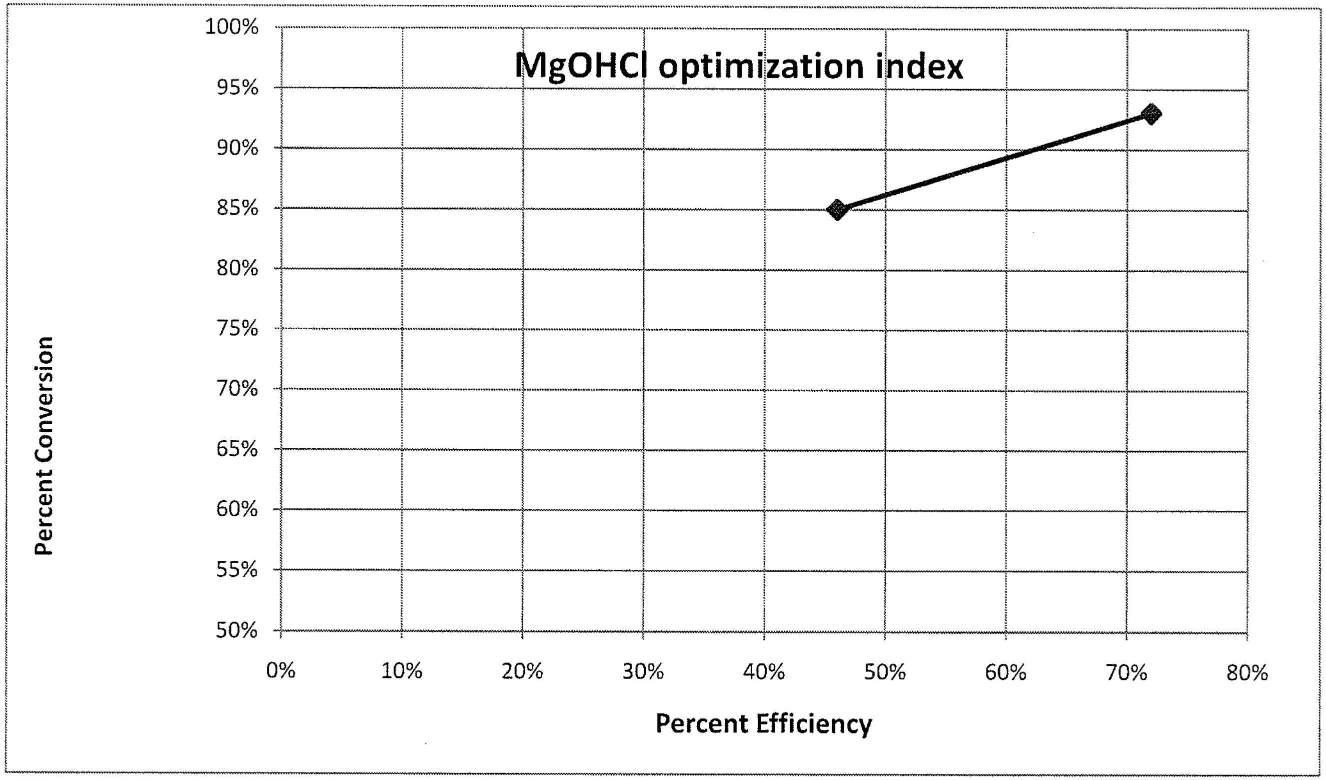
MgOHCl optimization index
Percent Conversion
100%
95%
90%
85%
80%
75%
70%
65%
60%
55%
50%
0%
10%
20%
30%
40%
50%
60%
70%
80%
Percent Efficiency

FIG. 36

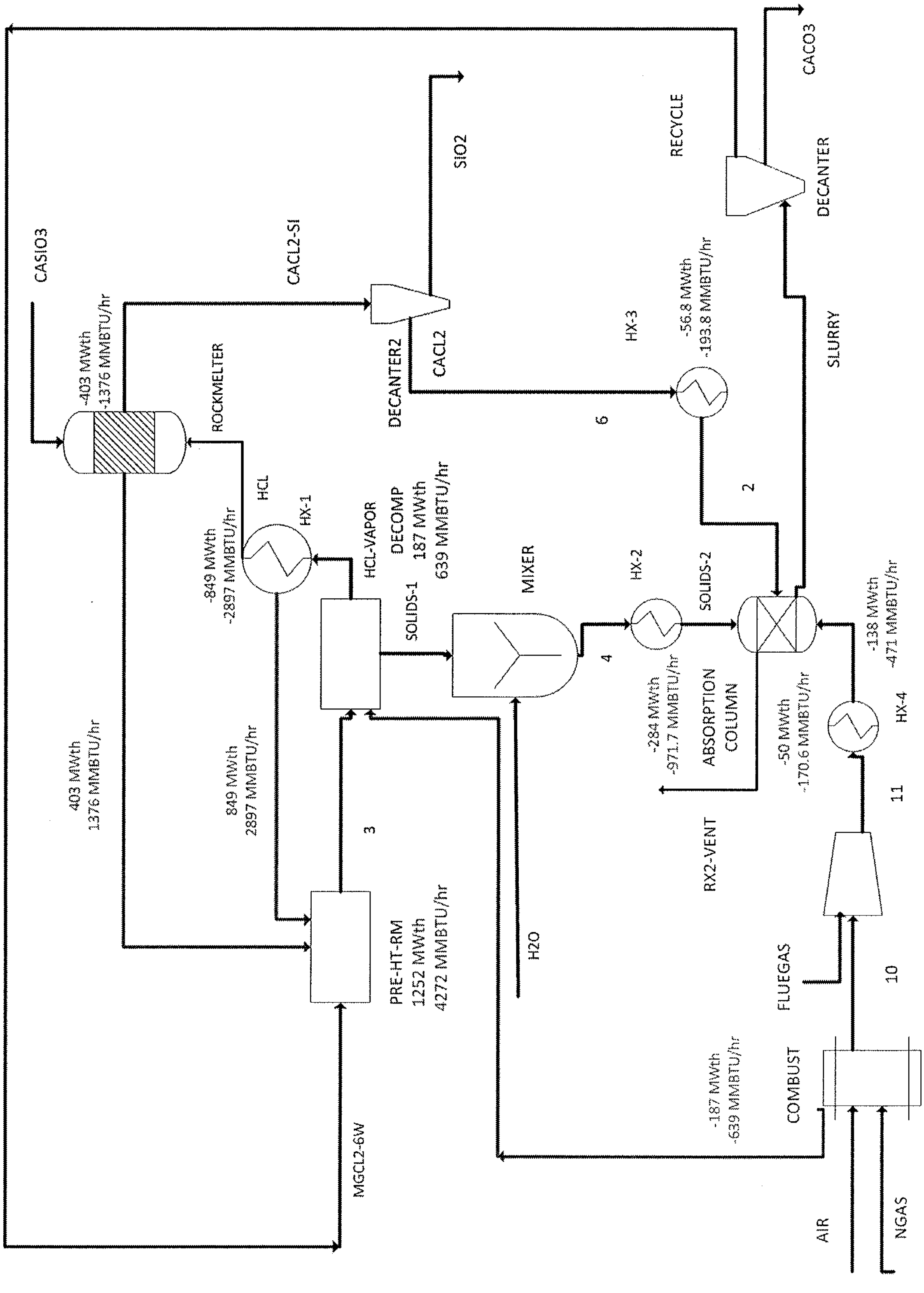
CASIO3
ROCKMELTER
-403 MWth
-1376 MMBTU/hr
CACL2-SI
DECANTER2
CACL2
SIO2
RECYCLE
CACO3
DECANTER
-56.8 MWth
-193.8 MMBTU/hr
HX-3
SLURRY
6
2
HCL
HX-1
-849 MWth
-2897 MMBTU/hr
HCL-VAPOR
DECOMP
187 MWth
639 MMBTU/hr
SOLIDS-1
MIXER
HX-2
SOLIDS-2
4
-284 MWth
-971.7 MMBTU/hr
ABSORPTION
COLUMN
-50 MWth
-170.6 MMBTU/hr
HX-4
-138 MWth
-471 MMBTU/hr
RX2-VENT
11
403 MWth
1376 MMBTU/hr
849 MWth
2897 MMBTU/hr
3
PRE-HT-RM
1252 MWth
4272 MMBTU/hr
H2O
FLUEGAS
10
-187 MWth
-639 MMBTU/hr
COMBUST
MGCL2-6W
AIR
NGAS

FIG. 37

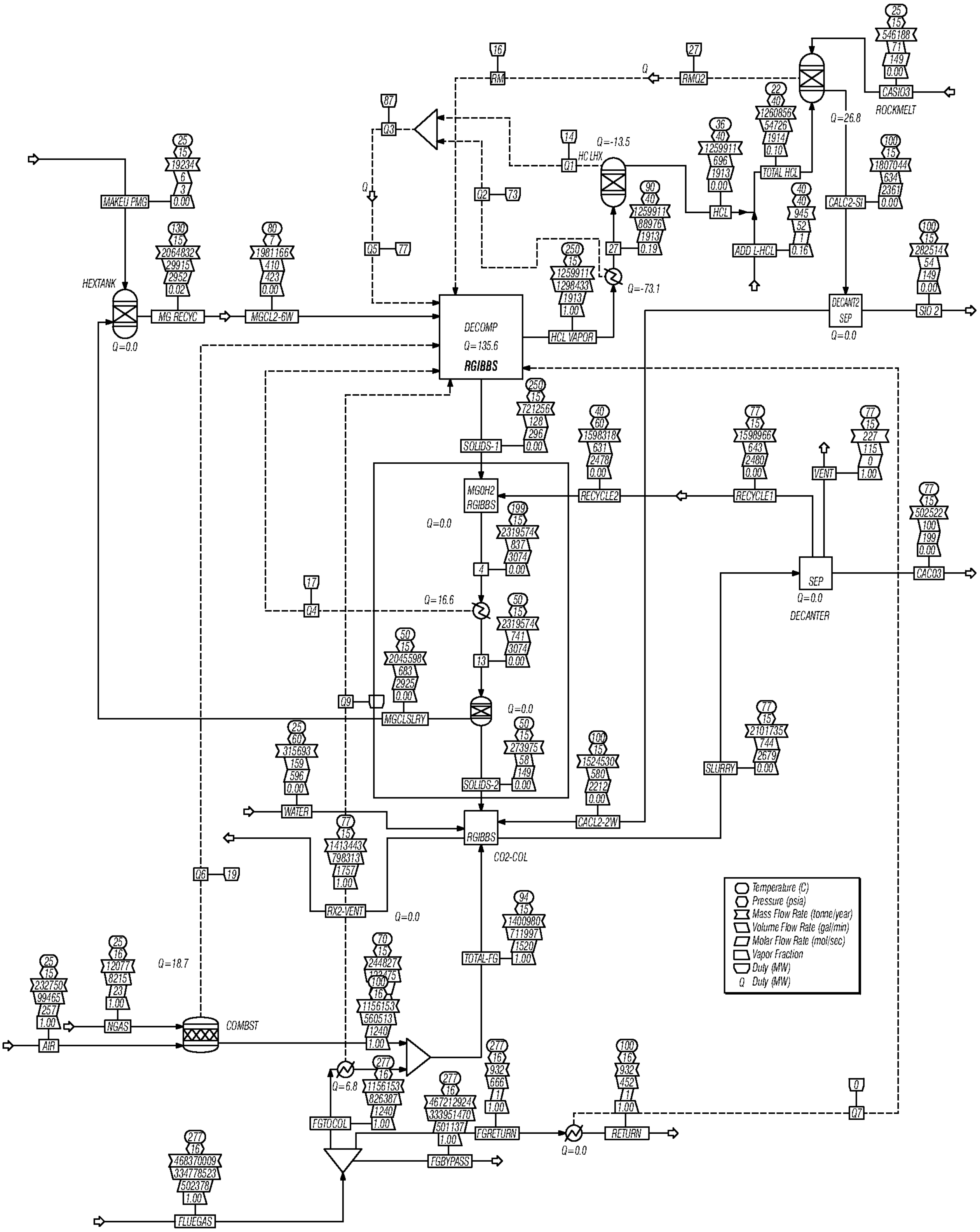
25
15
546188
71
149
0.00
CASIO3
ROCKMELT
16
RM
27
RMQ2
Q
87
Q3
Q
Q=26.8
22
40
1260856
54726
1914
0.10
TOTAL HCL
14
Q1
Q=-13.5
HCLHX
36
40
1259911
696
1913
0.00
HCL
100
15
1807044
634
2361
0.00
CALC2-SI
25
15
19234
6
3
0.00
MAKEU PMG
Q2
73
90
40
1259911
88976
1913
0.19
40
40
945
52
1
0.16
ADD L-HCL
Q5
77
27
Q=-73.1
250
15
1259911
1298433
1913
1.00
HCL VAPOR
130
15
2064832
29915
2952
0.02
80
7
1981166
410
423
0.00
HEXTANK
MG RECYC
MGCL2-6W
Q=0.0
DECOMP
Q=135.6
RGIBBS
DECANT2
SEP
Q=0.0
100
15
282514
54
149
0.00
SIO 2
250
15
721256
128
296
0.00
SOLIDS-1
40
60
1598318
631
2478
0.00
RECYCLE2
77
15
1598966
643
2480
0.00
RECYCLE1
77
15
227
115
0
1.00
VENT
MGOH2
RGIBBS
Q=0.0
199
15
2319574
837
3074
0.00
4
77
15
502522
100
199
0.00
CACO3
SEP
Q=0.0
DECANTER
17
Q4
Q=16.6
50
15
2319574
741
3074
0.00
13
50
15
2045598
683
2925
0.00
Q9
MGCLSLRY
Q=0.0
50
15
273975
58
149
0.00
SOLIDS-2
25
60
315693
159
596
0.00
WATER
100
15
1524530
580
2212
0.00
CACL2-2W
77
15
2101735
744
2679
0.00
SLURRY
77
15
1413443
798313
1757
1.00
RGIBBS
CO2-COL
RX2-VENT
Q=0.0
Q6
19
94
15
1400980
711997
1520
1.00
TOTAL-FG
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)
25
15
232750
99465
257
1.00
AIR
25
16
12077
8215
23
1.00
NGAS
Q=18.7
COMBST
70
15
244827
132475
100
16
1156153
560513
1240
1.00
Q=6.8
277
16
1156153
826387
1240
1.00
FGTOCOL
277
16
467212924
333951470
501137
1.00
FGRETURN
277
16
932
666
1
1.00
Q=0.0
100
16
932
452
1
1.00
RETURN
0
Q7
FGBYPASS
277
16
468370009
334778523
502378
1.00
FLUEGAS

FIG. 38A

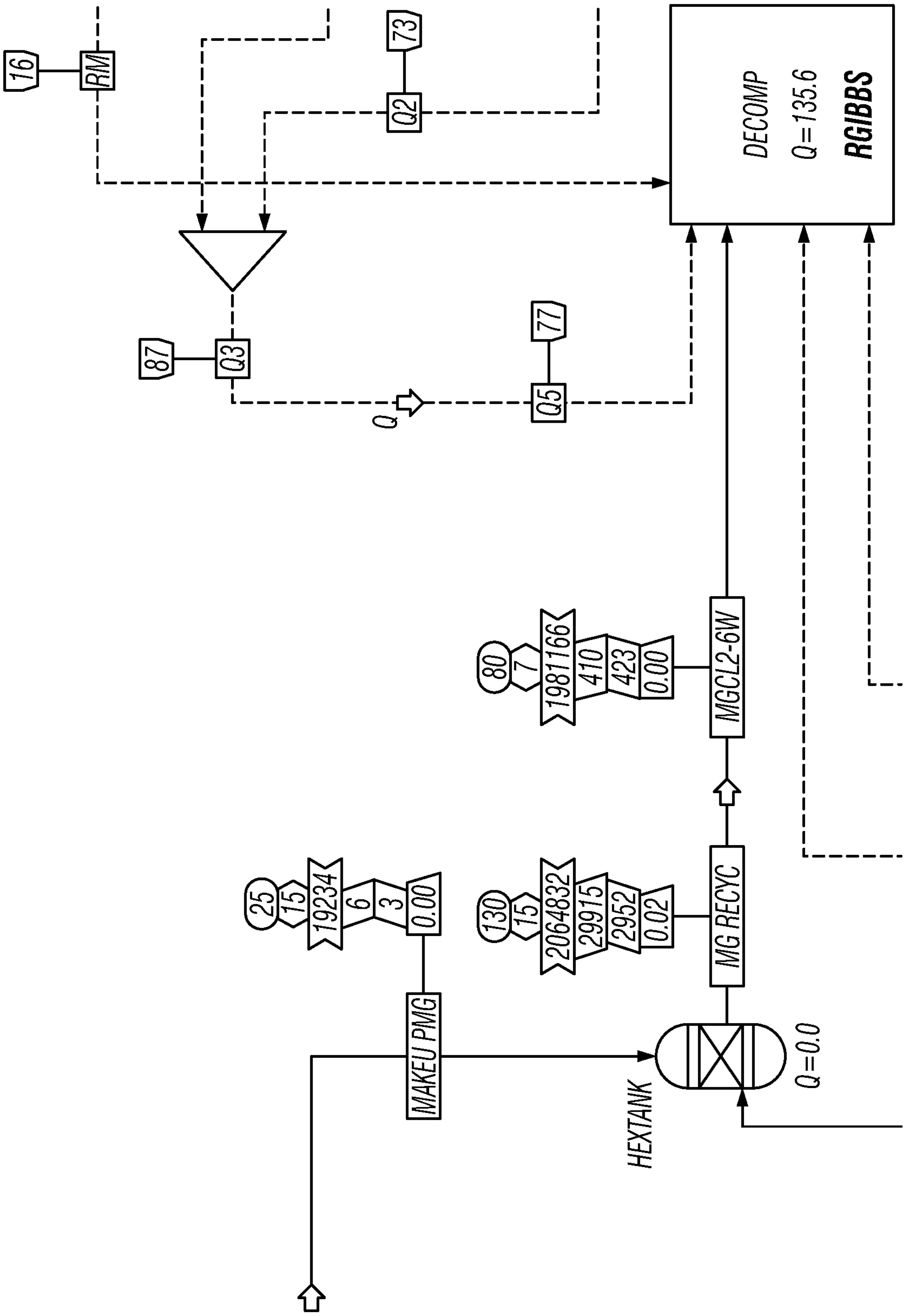
16
RM
73
Q2
DECOMP
Q=135.6
RGIBBS
87
Q3
77
Q5
Q
80
7
1981166
410
423
0.00
MGCL2-6W
25
15
19234
6
3
0.00
MAKEU PMG
130
15
2064832
29915
2952
0.02
MG RECYC
HEXTANK
Q=0.0

FIG. 38B

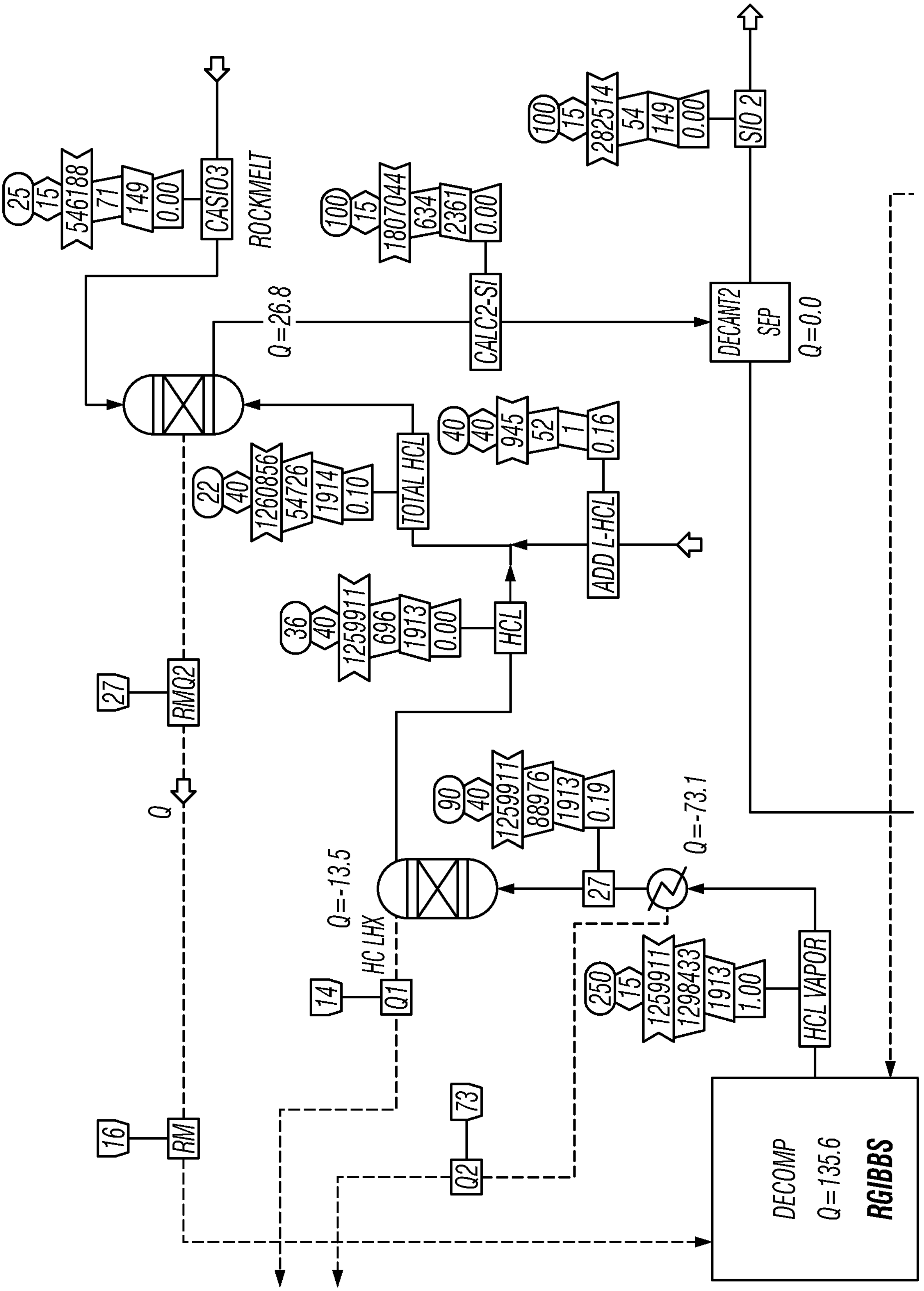
25
15
546188
71
149
0.00
CASIO3
ROCKMELT
100
15
1807044
634
2361
0.00
CALC2-SI
Q=-26.8
100
15
282514
54
149
0.00
SIO 2
DECANT2
SEP
Q=0.0
40
40
945
52
1
0.16
ADD L-HCL
22
40
1260856
54726
1914
0.10
TOTAL HCL
36
40
1259911
696
1913
0.00
HCL
27
RMQ2
Q
90
40
1259911
88976
1913
0.19
27
Q=-73.1
Q=-13.5
HC LHX
14
Q1
250
15
1259911
1298433
1913
1.00
HCL VAPOR
73
Q2
16
RM
DECOMP
Q=135.6
RGIBBS

FIG. 38C

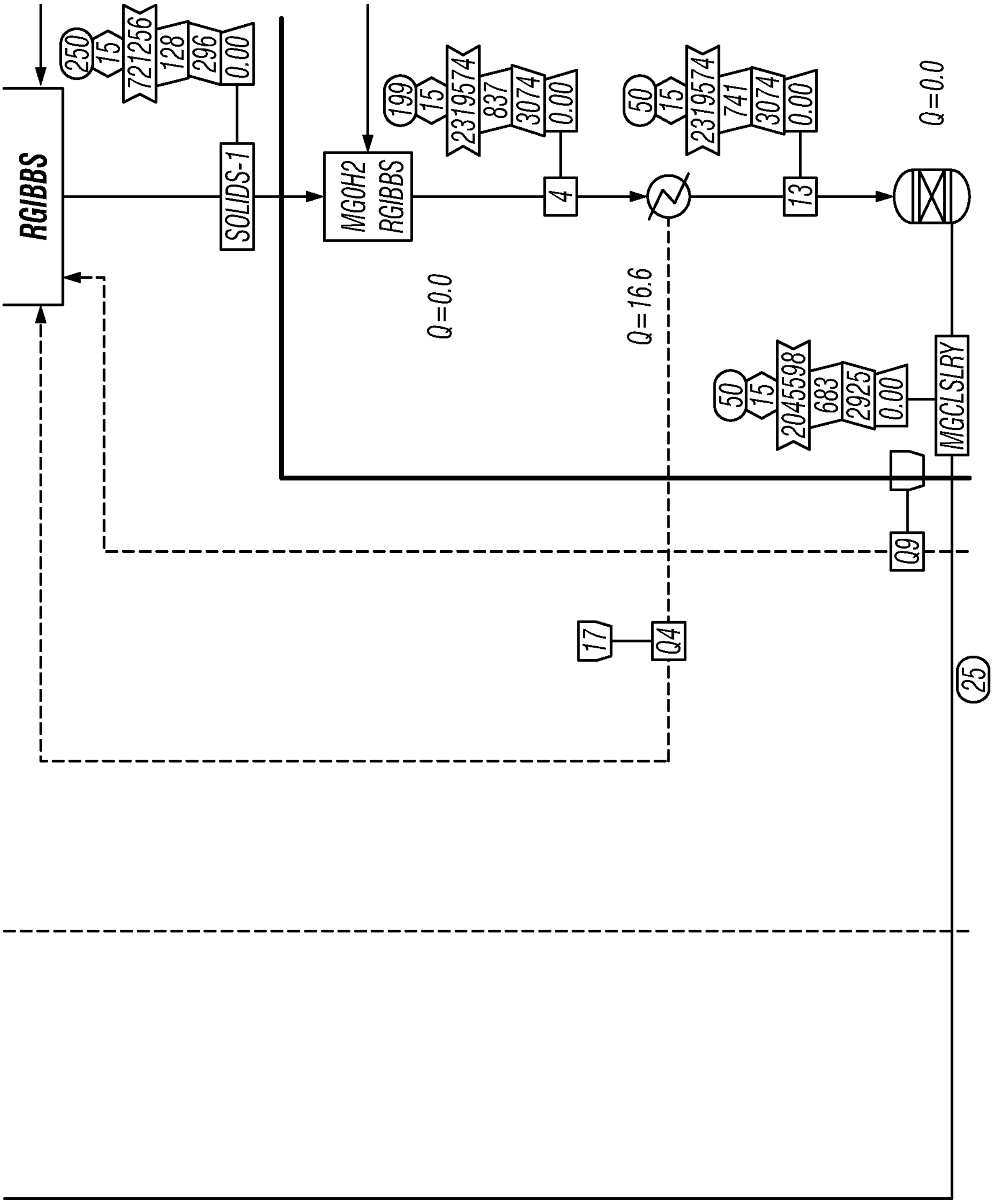
RGIBBS
250
15
721256
128
296
0.00
SOLIDS-1
MG0H2
RGIBBS
199
15
2319574
837
3074
0.00
4
Q=0.0
Q=16.6
50
15
2319574
741
3074
0.00
13
Q=0.0
50
15
2045598
683
2925
0.00
MGCLSLRY
Q9
17
Q4
25

FIG. 38D

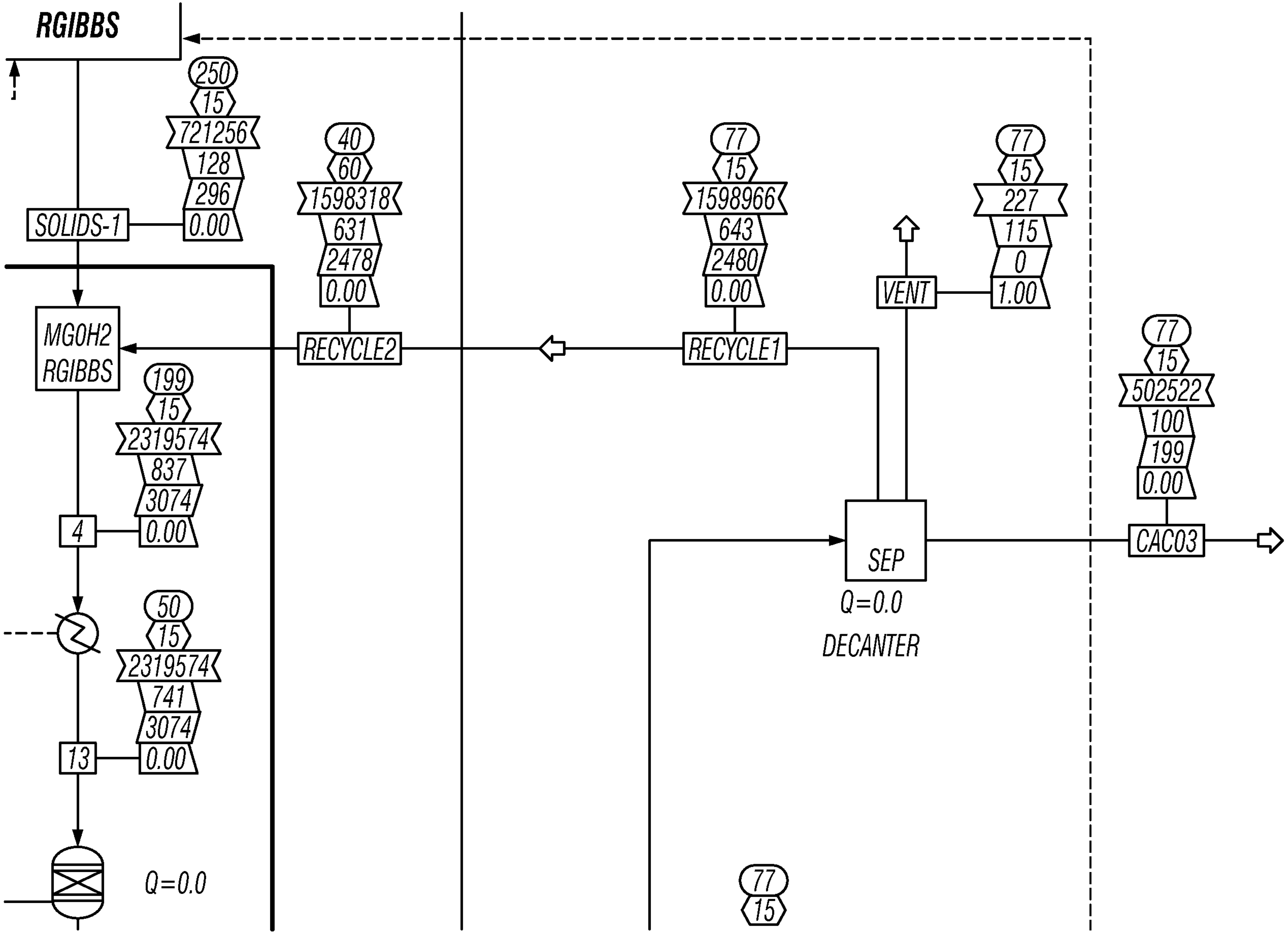
RGIBBS
250
15
721256
128
296
0.00
SOLIDS-1
MG0H2
RGIBBS
40
60
1598318
631
2478
0.00
RECYCLE2
199
15
2319574
837
3074
0.00
4
50
15
2319574
741
3074
0.00
13
Q=0.0
77
15
1598966
643
2480
0.00
RECYCLE1
77
15
227
115
0
1.00
VENT
SEP
Q=0.0
DECANTER
77
15
502522
100
199
0.00
CAC03
77
15

FIG. 38E

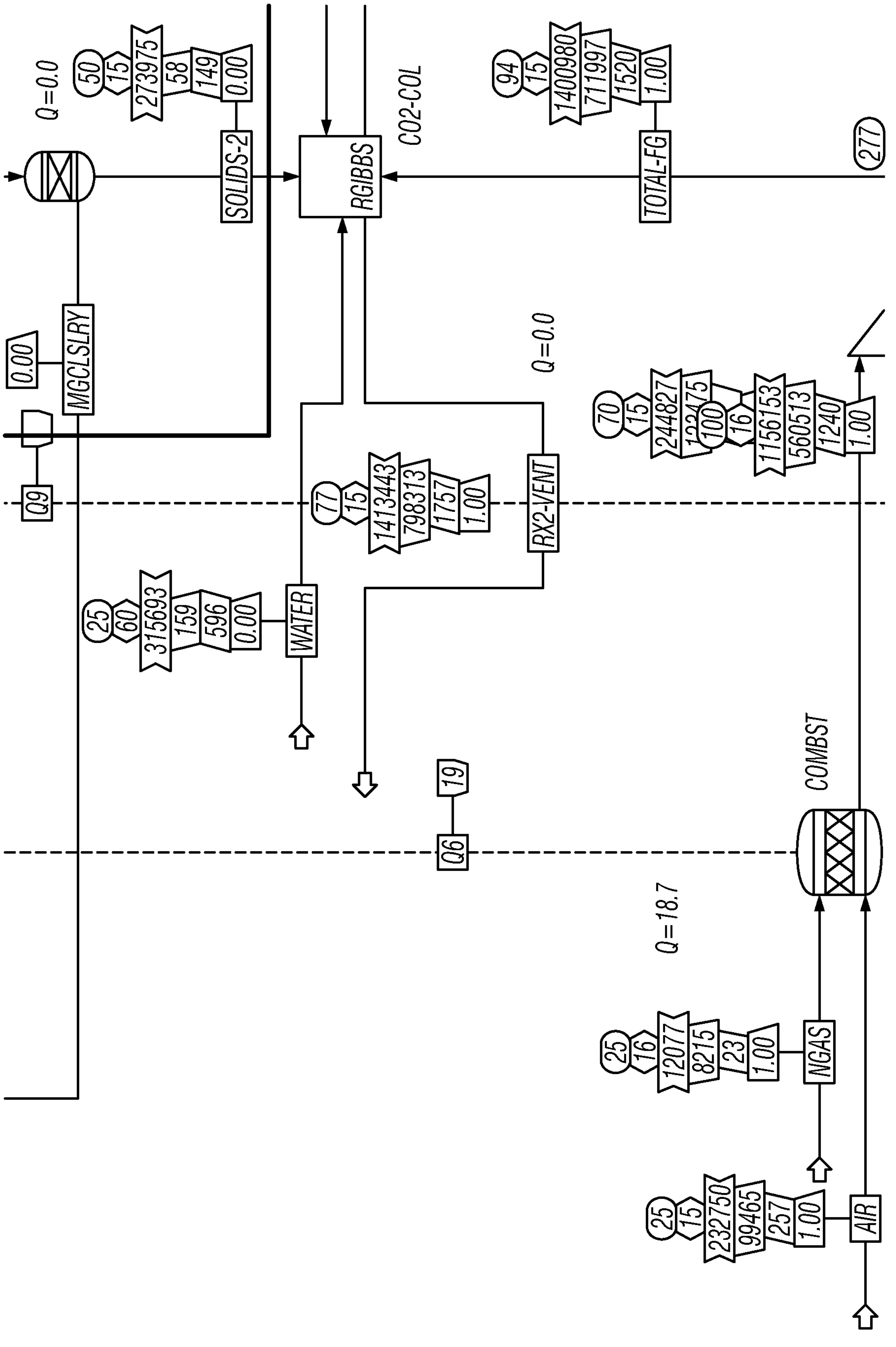
Q=0.0
50
15
273975
58
149
0.00
SOLIDS-2
RGIBBS
C02-COL
94
15
1400980
711997
1520
1.00
TOTAL-FG
277
0.00
MGCLSLRY
Q9
Q=0.0
77
15
1413443
798313
1757
1.00
RX2-VENT
70
15
244827
100
16
1156153
560513
1240
1.00
25
60
315693
159
596
0.00
WATER
19
Q6
COMBST
Q=18.7
25
16
12077
8215
23
1.00
NGAS
25
15
232750
99465
257
1.00
AIR

FIG. 38F

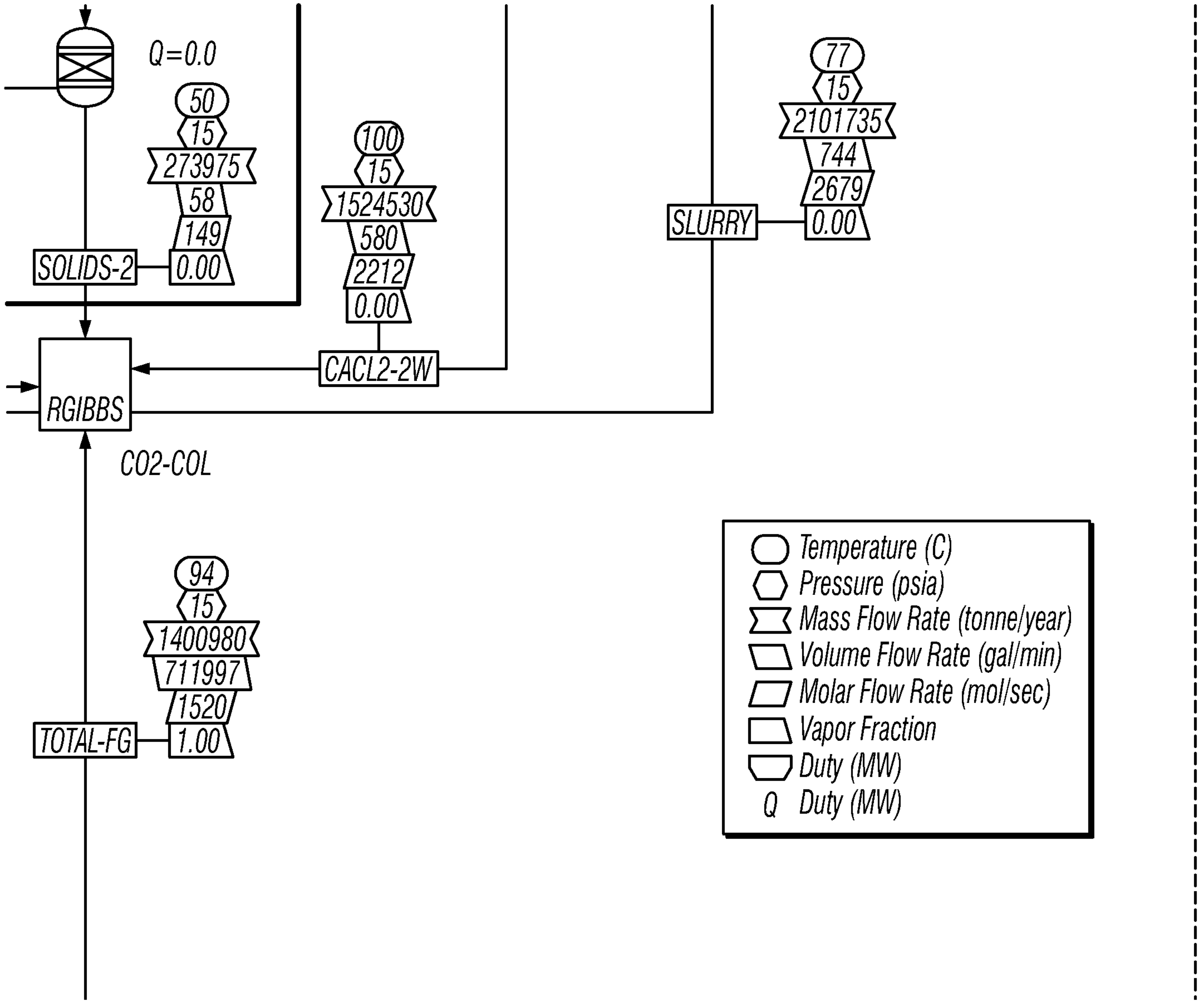
Q=0.0
50
15
273975
58
149
0.00
SOLIDS-2
100
15
1524530
580
2212
0.00
CACL2-2W
77
15
2101735
744
2679
0.00
SLURRY
RGIBBS
CO2-COL
94
15
1400980
711997
1520
1.00
TOTAL-FG
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Volume Flow Rate (gal/min)
Molar Flow Rate (mol/sec)
Vapor Fraction
Duty (MW)
Q Duty (MW)

FIG. 38G

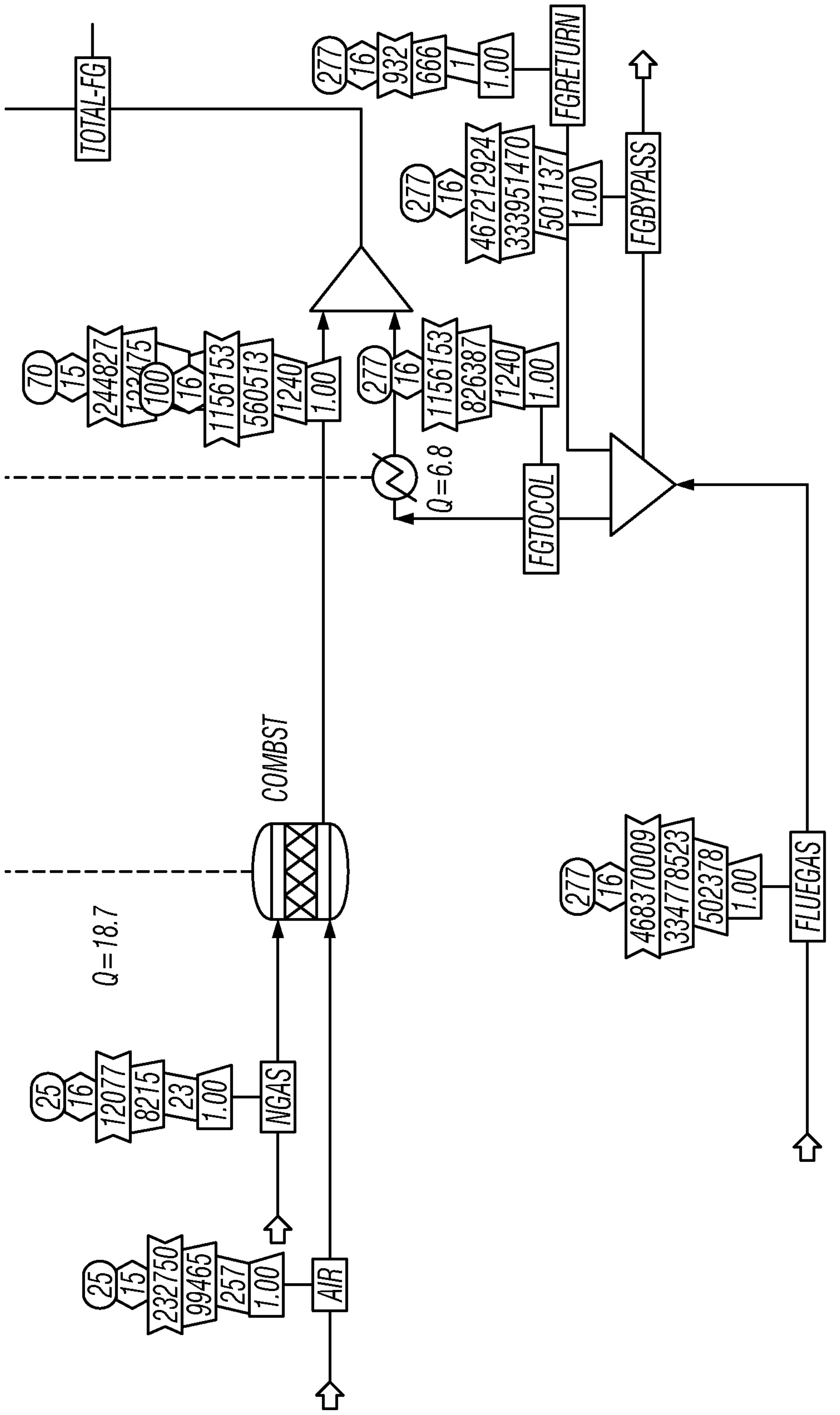
TOTAL-FG
277
16
932
666
1
1.00
FGRETURN
70
15
244827
122475
100
16
1156153
560513
1240
1.00
277
16
1156153
826387
1240
1.00
277
16
467212924
333951470
501137
1.00
FGBYPASS
Q=6.8
FGTOCOL
COMBST
Q=18.7
25
16
12077
8215
23
1.00
NGAS
25
15
232750
99465
257
1.00
AIR
277
16
468370009
334778523
502378
1.00
FLUEGAS

FIG. 38H

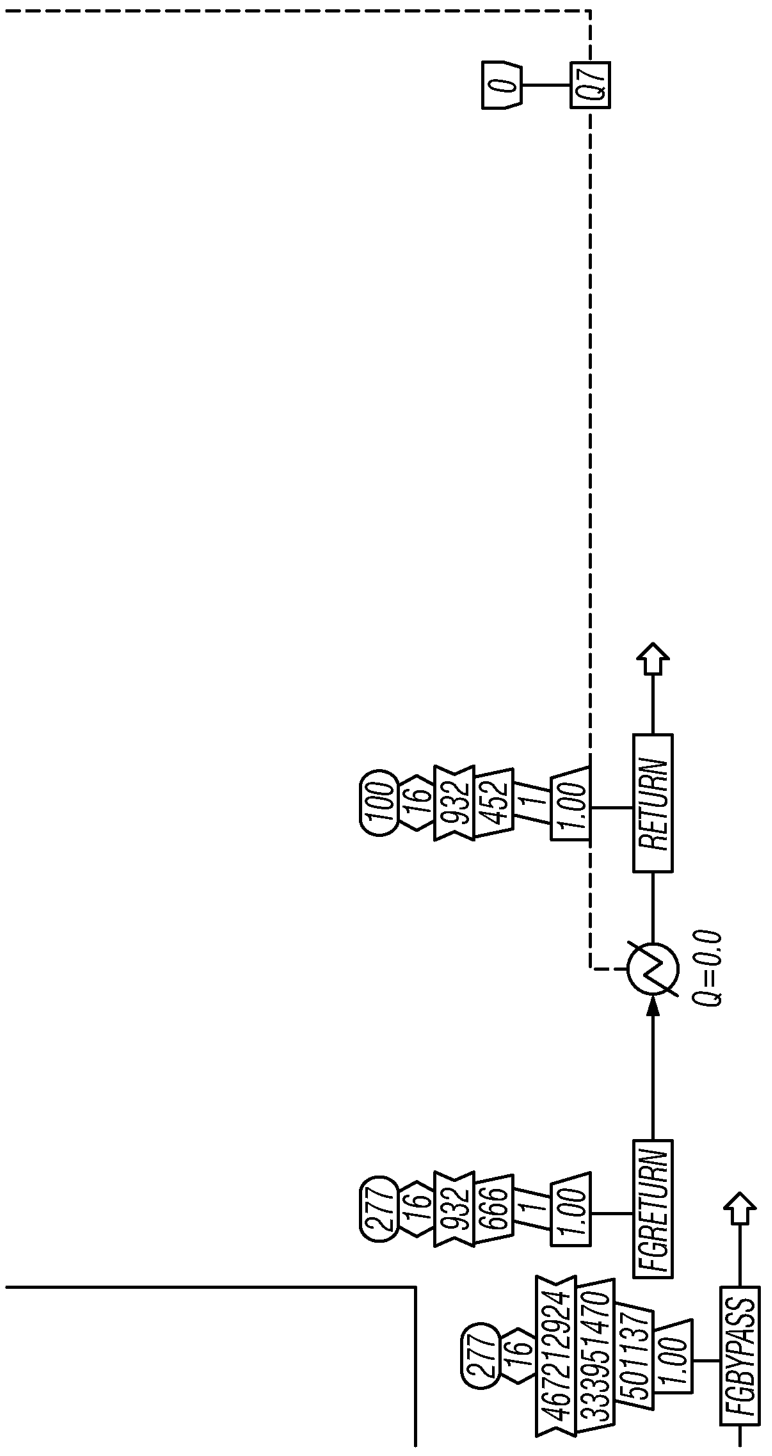
0
Q7
100
16
932
452
11
1.00
RETURN
Q=0.0
277
16
932
666
11
1.00
FGRETURN
277
16
467212924
333951470
501137
1.00
FGBYPASS

FIG. 38I

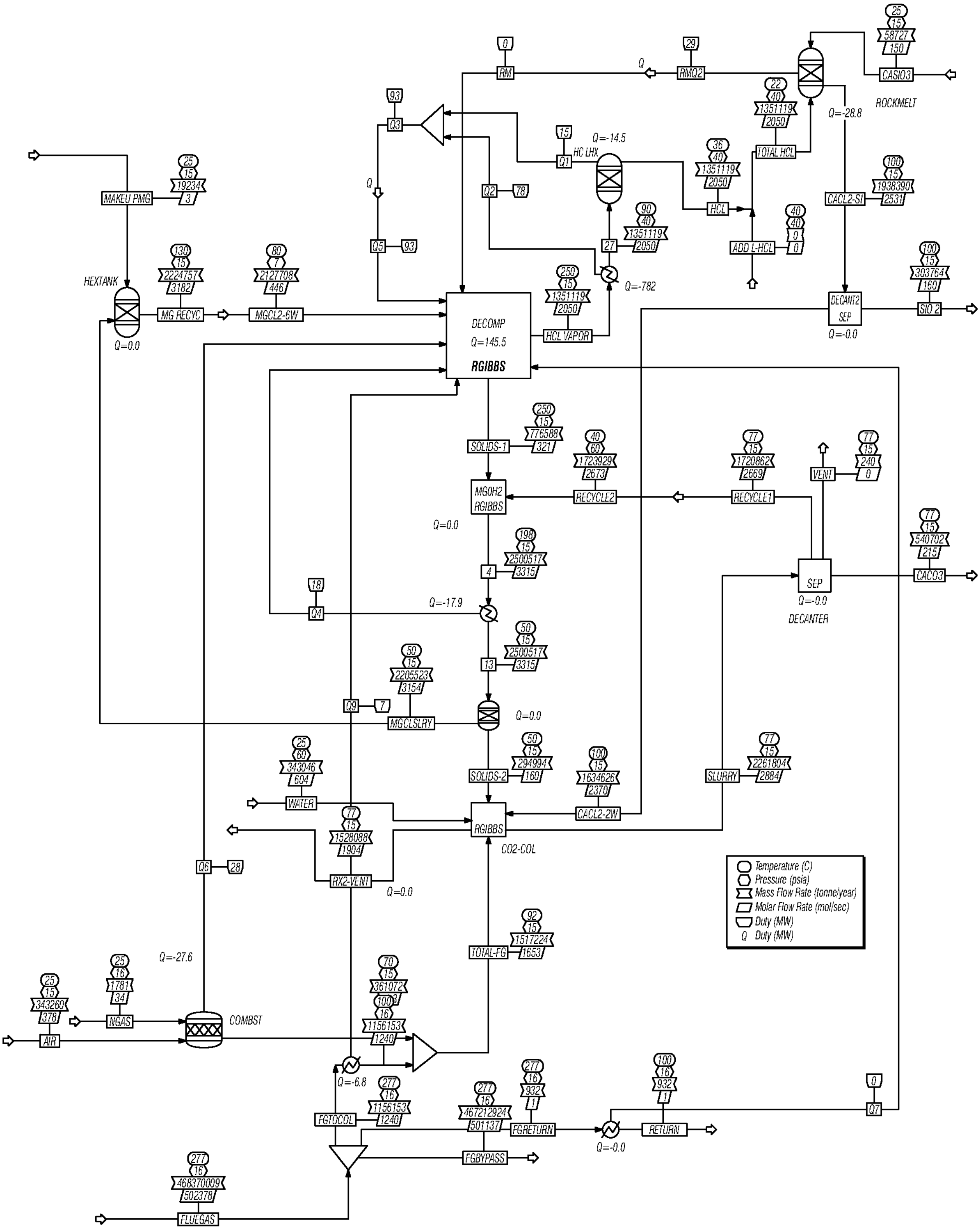
25
15
58727
150
CASIO3
ROCKMELT
0
RM
Q
29
RMQ2
22
40
1351119
2050
TOTAL HCL
Q=-28.8
93
Q3
15
Q1
Q=-14.5
HC LHX
36
40
1351119
2050
HCL
100
15
1938390
2531
CACL2-SI
Q
Q2
78
90
40
1351119
2050
27
ADD L-HCL
40
40
0
0
25
15
19234
3
MAKEU PMG
Q5
93
HEXTANK
130
15
2224757
3182
MG RECYC
80
7
2127708
446
MGCL2-6W
Q=0.0
250
15
1351119
2050
HCL VAPOR
Q=-782
DECOMP
Q=145.5
RGIBBS
DECANT2
SEP
Q=-0.0
100
15
303764
160
SIO 2
250
15
776588
321
SOLIDS-1
40
60
1723929
2673
RECYCLE2
77
15
1720862
2669
RECYCLE1
77
15
240
0
VENT
MG0H2
RGIBBS
Q=0.0
198
15
2500517
3315
4
77
15
540702
215
CACO3
SEP
Q=-0.0
DECANTER
18
Q4
Q=-17.9
50
15
2500517
3315
13
50
15
2205523
3154
Q9
7
MGCLSLRY
Q=0.0
50
15
294994
160
SOLIDS-2
100
15
1634626
2370
CACL2-2W
77
15
2261804
2884
SLURRY
25
60
343046
604
WATER
77
15
1528088
1904
RX2-VENT
Q=0.0
RGIBBS
CO2-COL
Q6
28
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Duty (MW)
Q Duty (MW)
92
15
1517224
1653
TOTAL-FG
Q=-27.6
25
15
343260
378
AIR
25
16
1781
34
NGAS
COMBST
70
15
361072
100
16
1156153
1240
Q=-6.8
277
16
1156153
1240
FGTOCOL
277
16
467212924
501137
277
16
932
1
FGRETURN
100
16
932
1
RETURN
Q=-0.0
0
Q7
FGBYPASS
277
16
468370009
502378
FLUEGAS

FIG. 39A

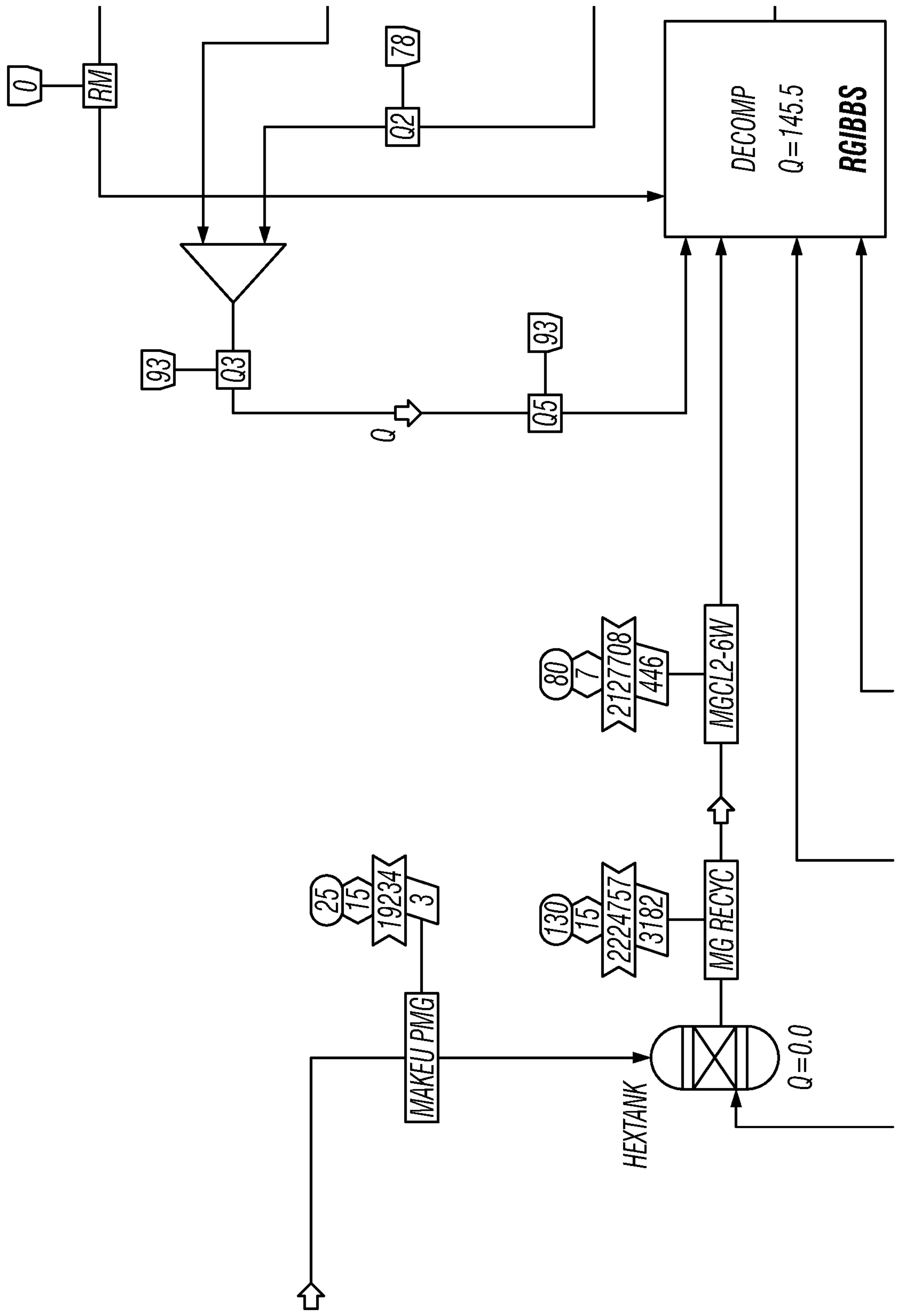
0
RM
78
Q2
93
Q3
Q
93
Q5
DECOMP
Q=145.5
RGIBBS
80
7
2127708
446
MGCL2-6W
25
15
19234
3
MAKEU PMG
130
15
2224757
3182
MG RECYC
HEXTANK
Q=0.0

FIG. 39B

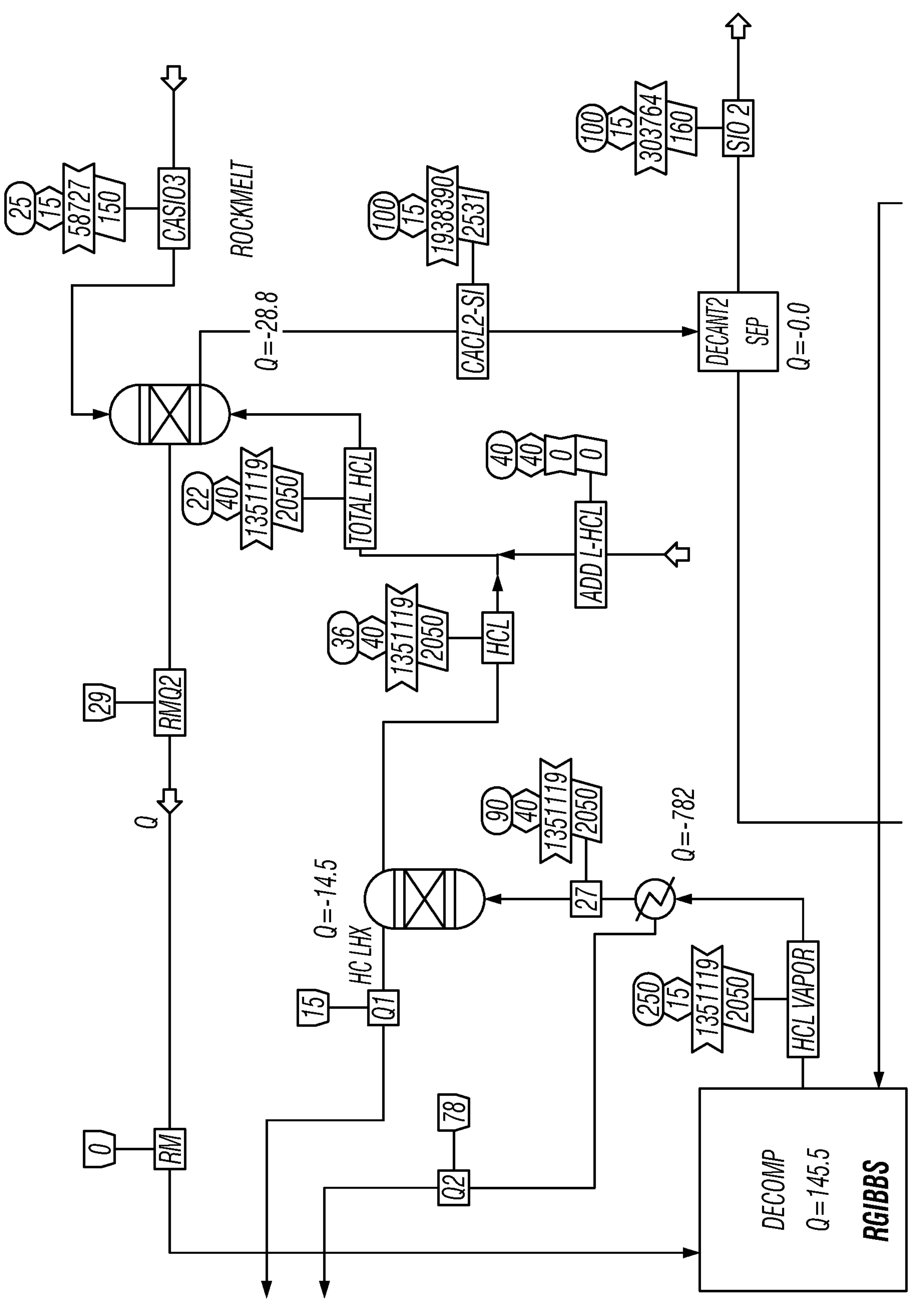
25
15
58727
150
CASIO3
ROCKMELT
Q=-28.8
100
15
1938390
2531
CACL2-SI
DECANT2
SEP
Q=-0.0
100
15
303764
160
SIO 2
22
40
1351119
2050
TOTAL HCL
40
40
0
0
ADD L-HCL
36
40
1351119
2050
HCL
29
RMQ2
Q
90
40
1351119
2050
Q=-782
27
Q=-14.5
HC LHX
15
Q1
250
15
1351119
2050
HCL VAPOR
0
RM
78
Q2
DECOMP
Q=145.5
RGIBBS

FIG. 39C

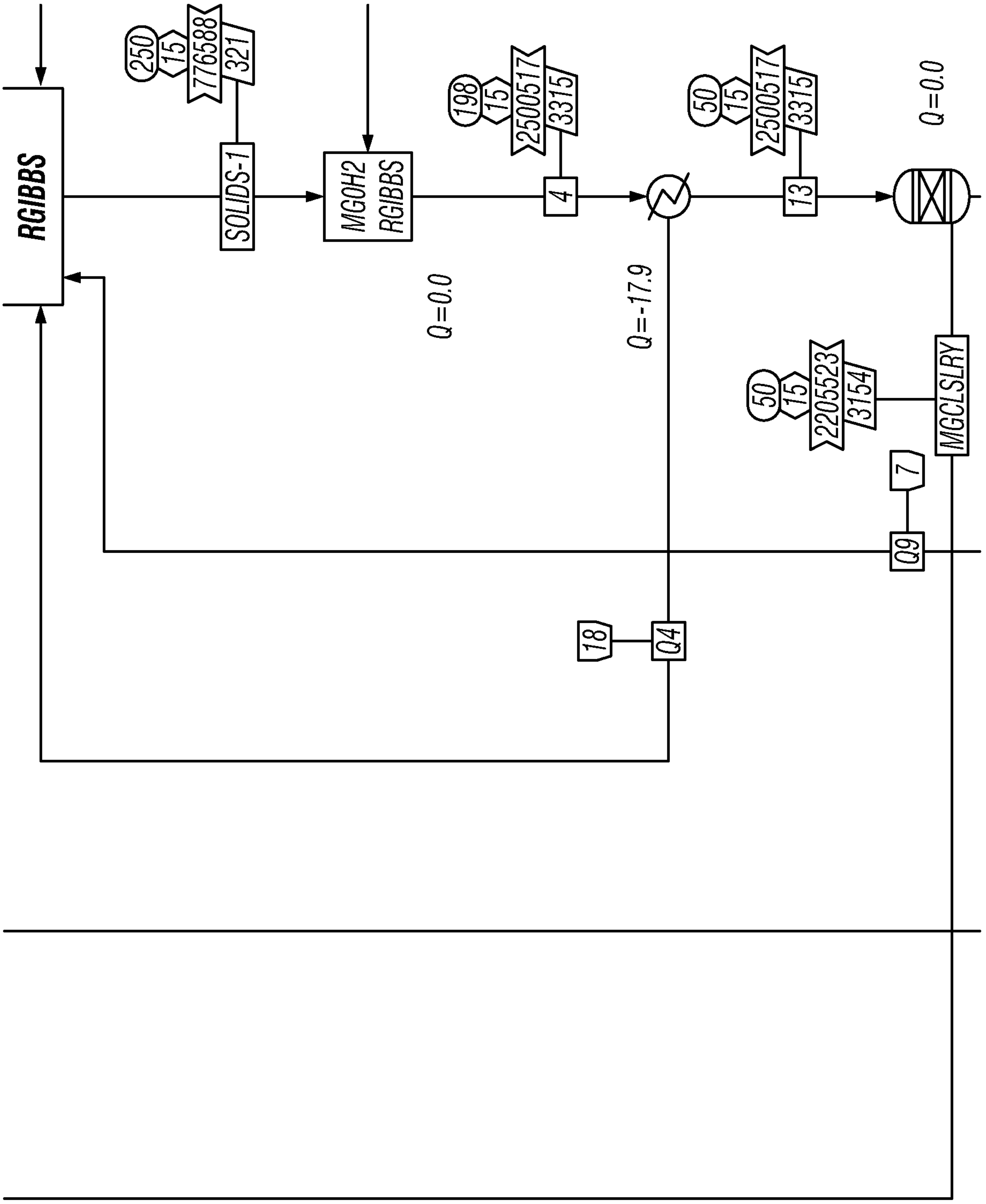
RGIBBS
250
15
776588
321
SOLIDS-1
MG0H2
RGIBBS
Q=0.0
198
15
2500517
3315
4
Q=-17.9
50
15
2500517
3315
13
Q=0.0
50
15
2205523
3154
MGCLSLRY
7
Q9
18
Q4

FIG. 39D

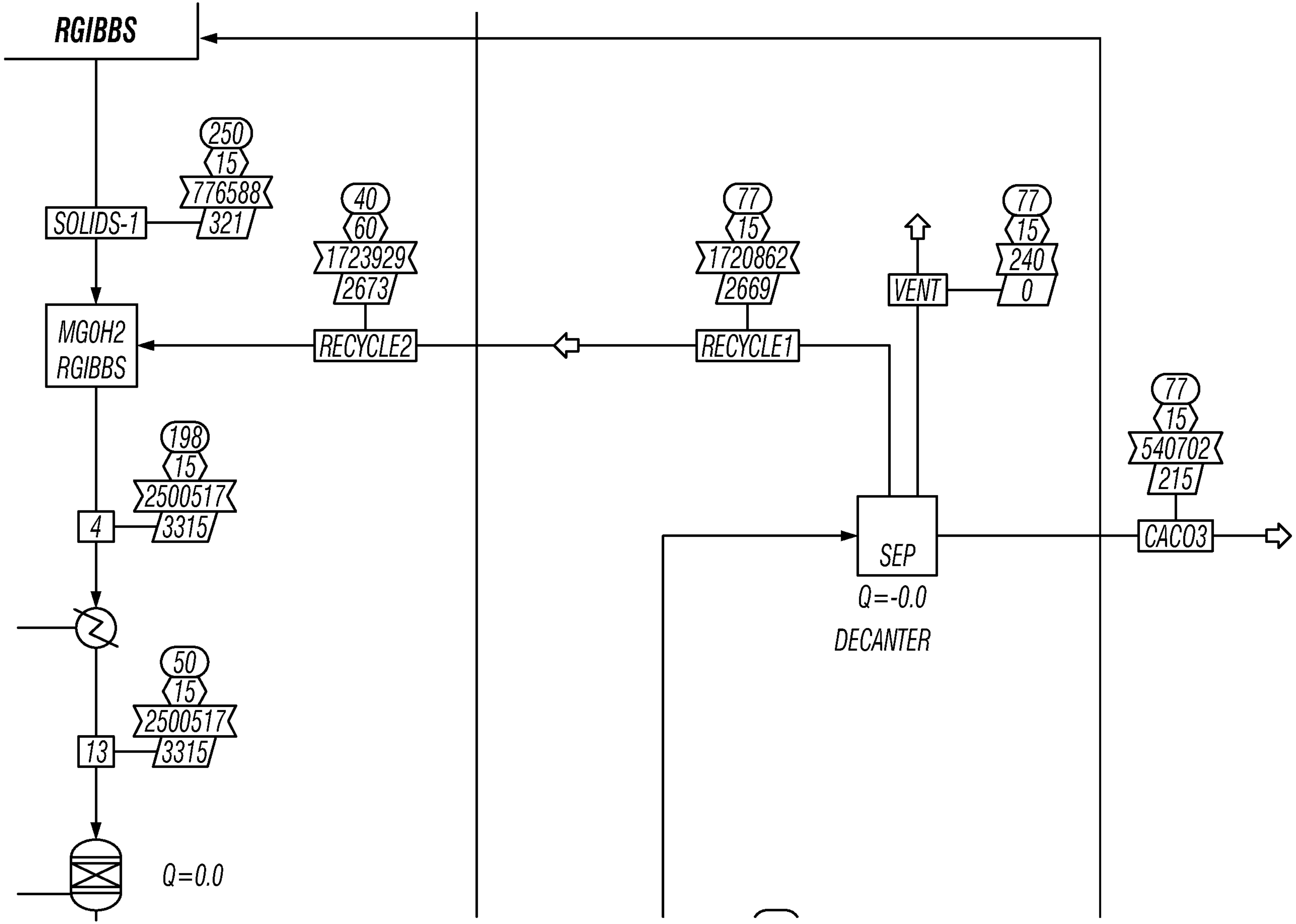
RGIBBS
250
15
776588
321
SOLIDS-1
MG0H2
RGIBBS
40
60
1723929
2673
RECYCLE2
77
15
1720862
2669
RECYCLE1
VENT
77
15
240
0
198
15
2500517
3315
4
SEP
Q=-0.0
DECANTER
77
15
540702
215
CACO3
50
15
2500517
3315
13
Q=0.0

FIG. 39E

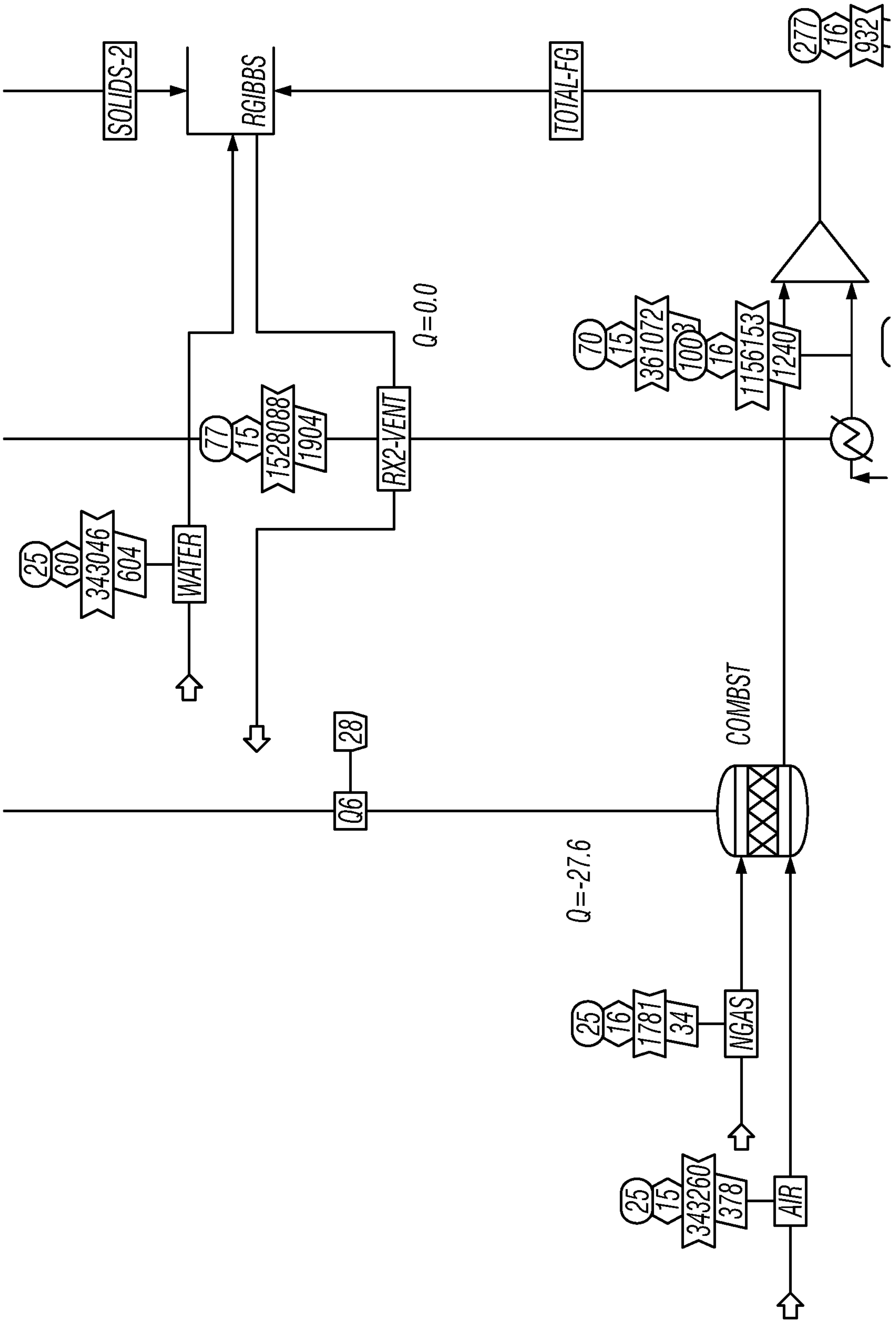
SOLIDS-2
RGIBBS
TOTAL-FG
277
16
932
Q=0.0
70
15
361072
3
100
16
1156153
1240
77
15
1528088
1904
RX2-VENT
25
60
343046
604
WATER
28
Q6
COMBST
Q=-27.6
25
16
1781
34
NGAS
25
15
343260
378
AIR

FIG. 39F

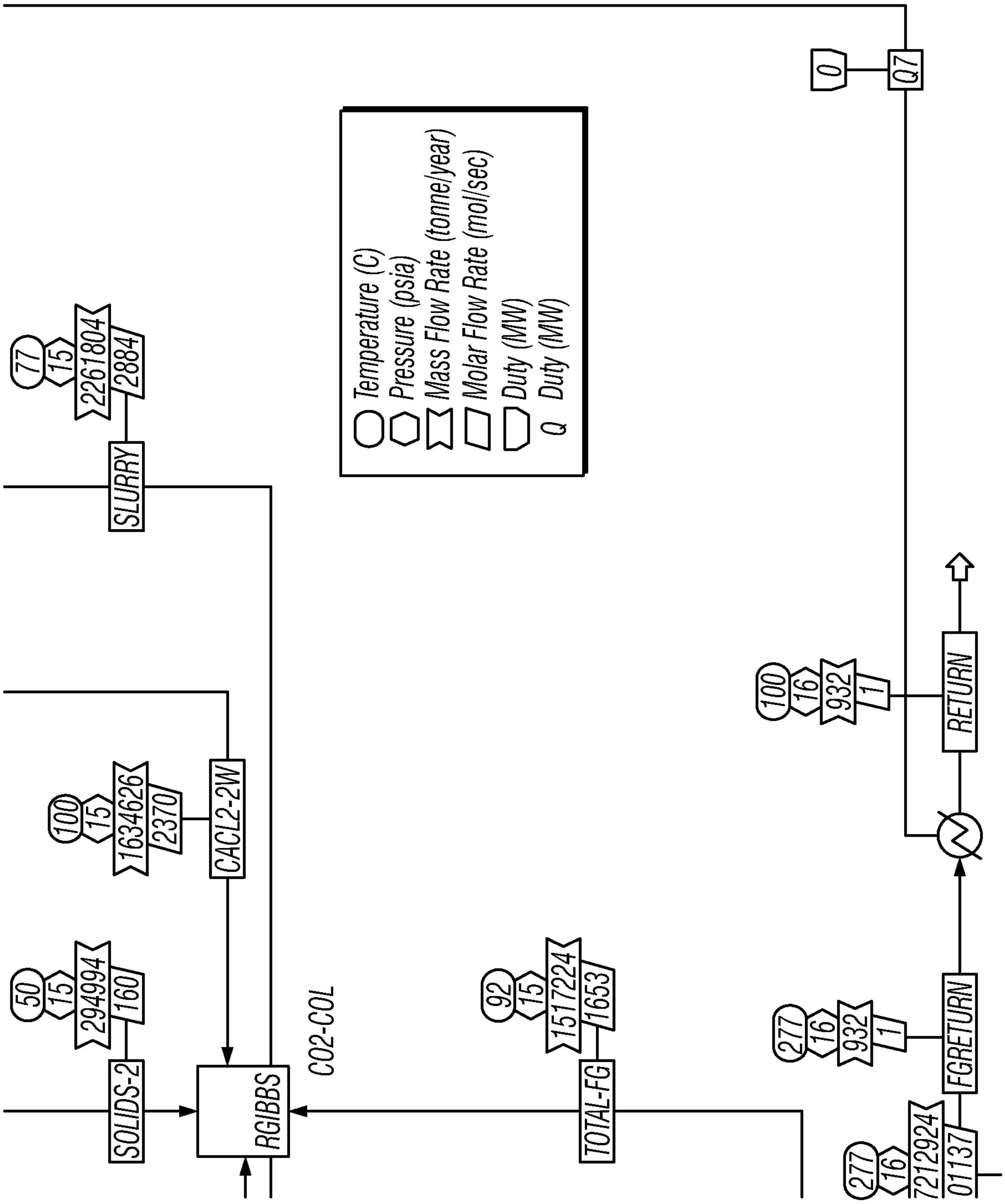
Temperature (C)
Pressure (psia)
Mass Flow Rate (tonne/year)
Molar Flow Rate (mol/sec)
Duty (MW)
Q Duty (MW)
77
15
2261804
2884
SLURRY
100
15
1634626
2370
CACL2-2W
50
15
294994
160
SOLIDS-2
RGIBBS
CO2-COL
92
15
1517224
1653
TOTAL-FG
0
Q7
100
16
932
1
RETURN
277
16
932
1
FGRETURN
277
16
7212924
01137

FIG. 39G

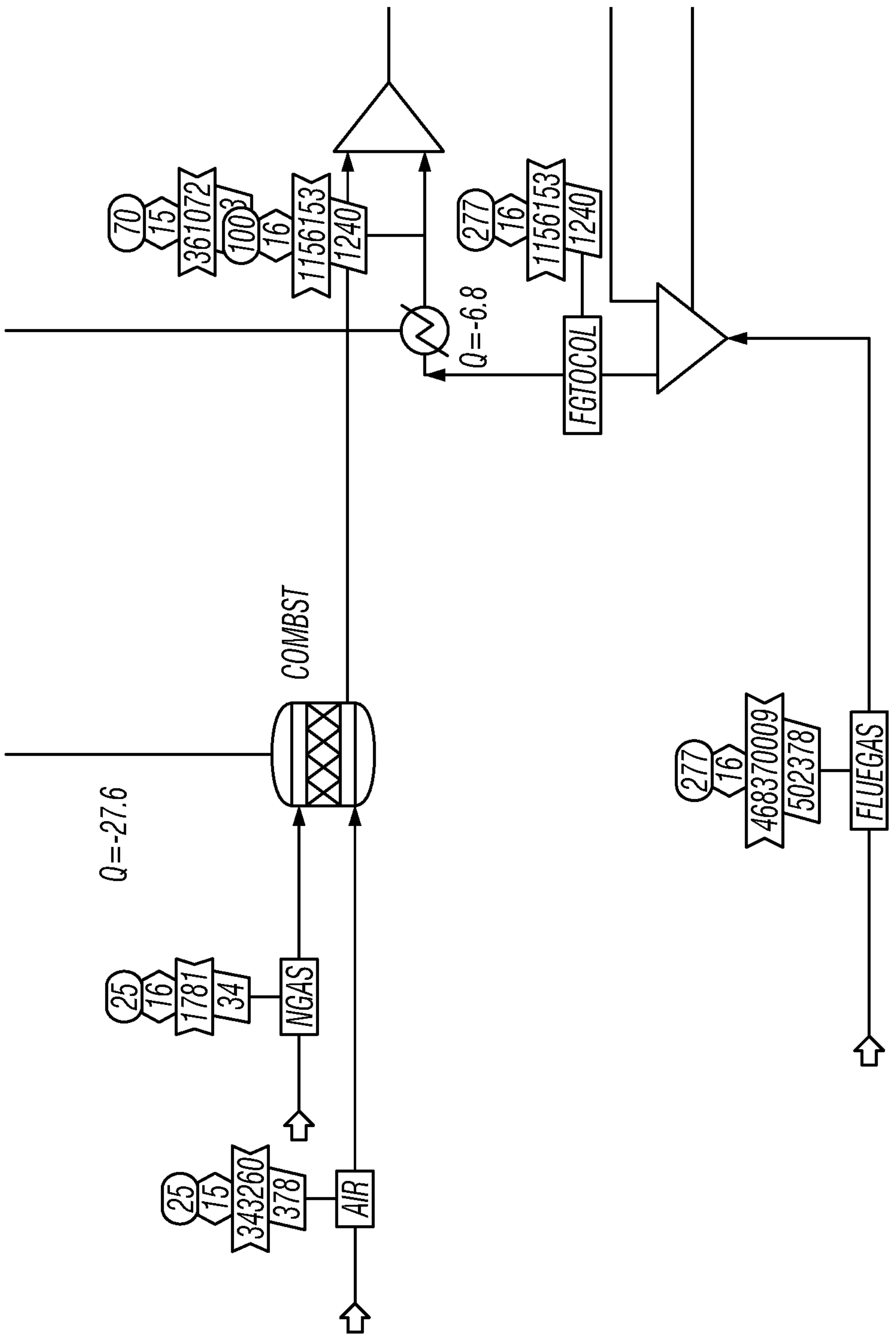
AIR
25
15
343260
378
NGAS
25
16
1781
34
Q=-27.6
COMBST
70
15
361072
3
100
16
1156153
1240
Q=-6.8
277
16
1156153
1240
FGTOCOL
277
16
468370009
502378
FLUEGAS

FIG. 39H

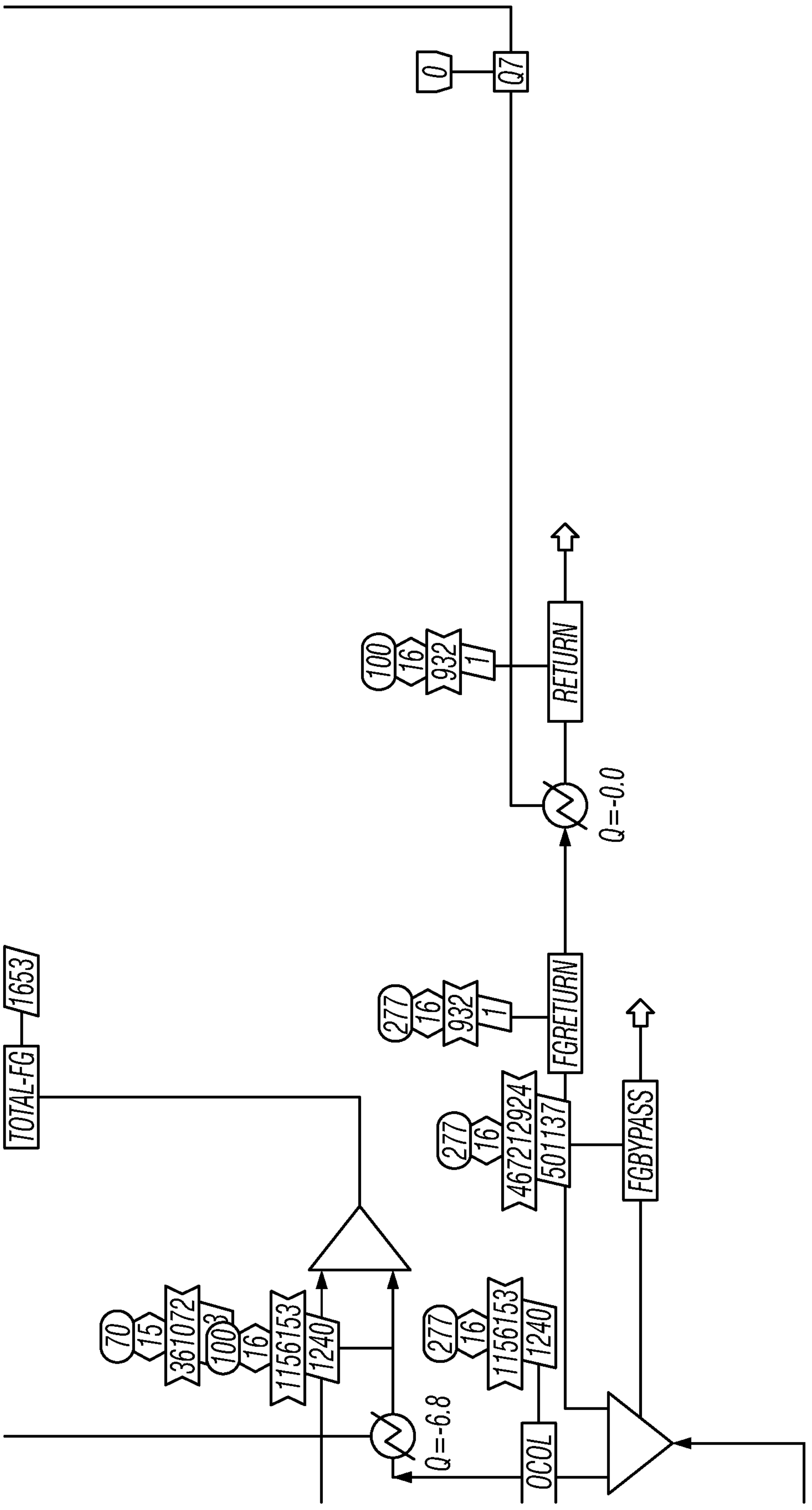
Q7
0
100
16
932
1
RETURN
Q=-0.0
TOTAL-FG
1653
277
16
932
1
FGRETURN
277
16
467212924
501137
FGBYPASS
70
15
361072
3
100
16
1156153
1240
Q=-6.8
277
16
1156153
1240
OCOL

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, magensium 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.