DESCRIPTION

CARBON DIOXIDE SEQUESTRATION INVOLVING TWO-SALT-BASED THERMOLYTIC PROCESSES

BACKGROUND OF THE INVENTION

The present application claims priority to U.S. Provisional Application Serial Nos. 61/362,607, filed July 8, 2010, 61/370,030, filed August 2, 2010, 61/406,536, filed October 25, 2010, and 61/451,078, filed March 9, 2011~~, the entire contents of each of which are incorporated herein by reference in their 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

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

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 MgCl2.6H2O by DTA and TG – Y. Kirsh, S. Yariv and S. Shoval – Journal of Thermal Analysis, Vol. 32 (1987)~~, both of which are incorporated herein by reference in their entireties~~.

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:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \quad (26)$$

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

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~~.

U.S. Prov. Appln. 60/612,355

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

U.S. Prov. Appln. 61/362,607

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Goldberg *et al.*, *Proceedings of First National Conference on Carbon Sequestration, 14–17 May 2001, Washington, DC.*, section 6c,United States Department of Energy, National Energy Technology Laboratory. available at: http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/6c1.pdf.

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.