

Carbonation of Calcium Silicates for Long-Term CO₂ Sequestration

[Note: This document was prepared for attachment to a provisional patent application submitted to the United States Patent and Trademark Office on 4/23/03.]

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1. Brief Description of the Invention

A novel, three-step chemical process achieves CO₂ capture, separation and sequestration in a single, integrated operation. In step 1, aqueous caustic soda (NaOH) reacts with a solid, calcium-rich silicate feedstock to produce crystalline portlandite [Ca(OH)₂] or crystalline sodium-calcium hydroxysilicate [NaCaSiO₃(OH)] ± crystalline hydroxy-sodalite [Na₈(AlSiO₄)₆(OH)₂] ± residual aluminosilicate material. In step 2, CO₂-bearing flue gas (or pure CO₂ already captured and separated from flue gas) is bubbled into a NaOH-bearing aqueous liquid, creating aqueous ± crystalline sodium carbonate (Na₂CO₃) + water (H₂O). In step 3, the Na₂CO₃ generated in step 2 is reacted with the crystalline hydroxide(s) produced in step 1 to form crystalline calcite (CaCO₃) ± crystalline carbonate-cancrinite [Na₈(AlSiO₄)₆CO₃·2H₂O] + aqueous NaOH. The aqueous NaOH is subsequently recycled to create additional Na₂CO₃ in step 2. Results of exploratory autoclave experiments indicate that all dissolution/precipitation reactions proceed rapidly at 200°C and pressures < 15 atm. Both calcite and carbonate-cancrinite are thermodynamically stable, environmentally benign, and sparingly soluble in meteoric water.

2. Background

Rising levels of carbon dioxide (CO₂) in the Earth's atmosphere, caused primarily by combustion of fossil fuels, have prompted concern that temperatures at the Earth's surface will increase sharply during the 21st century. To address this issue, numerous nations are developing plans for lowering CO₂ emissions to the atmosphere. The principal approaches under

consideration are: improving energy efficiency; making greater use of alternative sources of energy; and developing economically viable technologies for capture, separation, and long-term storage of CO₂. The latter strategy, known as “CO₂ sequestration,” is receiving increasing attention because it permits continued use of high-carbon fossil fuels to generate electrical power while ensuring that CO₂ releases to the atmosphere are reduced.

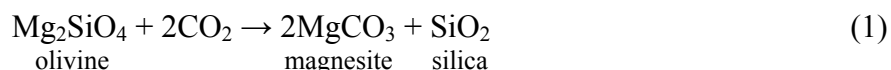
A potentially attractive means for *geological* CO₂ sequestration is injection of gaseous CO₂ into underground reservoirs—e.g., active or depleted oil and gas fields, deep brine formations, and deep, unmineable coal beds^(1,2). The underlying premise of this approach is that, after injection, the CO₂ will remain sequestered in the host rock for hundreds, perhaps even thousands, of years. In practice, however, such long-term reservoir integrity cannot be guaranteed. If either gaseous CO₂ or CO₂-saturated formation water escapes to overlying strata or to the surface, underground and subaerial water supplies could become seriously contaminated, and/or large amounts of CO₂ could be released to the atmosphere.

Significantly, the reservoir-integrity problems associated with geological sequestration of gaseous or liquid CO₂ can be completely avoided by chemically binding CO₂ with suitable solid materials⁽³⁻⁸⁾. This alternative CO₂ sequestration strategy, known as “mineral carbonation,” involves reaction of CO₂ with naturally occurring silicates to produce solid carbonate compounds, such as calcite (CaCO₃) and magnesite (MgCO₃), for the purpose of long-term terrestrial isolation of CO₂. “Mineral carbonation” also implies a chemical process carried out at elevated temperatures and pressures in an industrial-scale reactor, because a similar term, “mineral trapping,” alludes to crystallization of carbonate compounds at ambient temperature and pressure after CO₂ is injected into a subsurface geologic formation. The U.S. Department of Energy (DOE) classifies mineral carbonation as a “CO₂ conversion” technology—rather than a geological CO₂-sequestration strategy—because in mineral carbonation, most, if not all, of the CO₂ is converted to one or more solid carbonate compounds, whereas in mineral trapping only a tiny fraction (generally less than one volume %) of the injected CO₂ is ultimately incorporated into solid carbonates⁽²⁾.

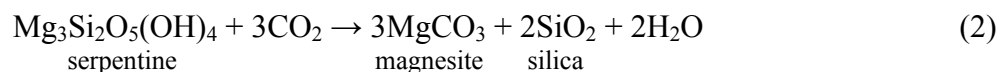
Mineral carbonation has many important advantages over alternative methods for large-scale CO₂ sequestration⁽³⁻⁸⁾. First, the carbonate compounds and residual silicate(s) or aluminosilicate(s) formed in the process are thermodynamically stable, environmentally benign, and weakly soluble in meteoric water. Consequently, they can be amended to soils to reduce acidity and increase moisture content, combined with stone to strengthen roadbeds, or simply dumped in a landfill. Alternatively, the materials could be returned to the site of excavation to fill the cavity created by soil/rock removal. Regardless of the particular end use or disposal scheme selected for the carbonates, the reacted CO₂ will remain tightly bound in the crystallographic structures of the carbonates—immobilized for an indefinite period of time. Therefore, a commercial mineral carbonation technology creates no major “legacy issues” for nearby population centers. In contrast, other proposed methods for wide-scale CO₂ sequestration—such as subsurface storage in brine formations, and disposal in deep-ocean realms—rely on risky

environmental factors to ensure long-term CO₂ containment: an impervious, superjacent “caprock” in the case of subsurface injection of CO₂ into brine formations, and low ambient temperature and high ambient pressure, with no current-driven dispersal of the sequestration “agent” (liquid CO₂ or CO₂-hydrate), in the case of suboceanic CO₂ disposal.

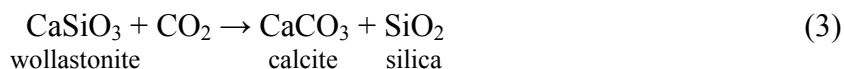
In weighing the technical feasibility of CO₂ sequestration by mineral carbonation, it should be noted that huge masses of rocks and clay-rich formations suitable for carbonation occur worldwide. For example, ultramafic complexes and large serpentinite bodies are major sources of the magnesium-rich minerals olivine and serpentine⁽⁹⁻¹²⁾, which can be carbonated by the reactions



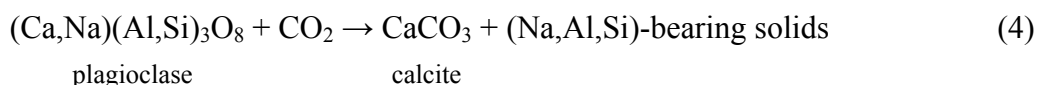
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Moreover, contact-metamorphosed limestones frequently contain wollastonite (CaSiO₃), and large quantities of plagioclase [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x})O₈] are present in many different types of common rocks. Wollastonite and plagioclase are converted to calcite (plus silicious solid material) by the nominal reactions



and



Another key attribute of mineral carbonation, in relation to other technologies that deal with CO₂ waste streams, is that costs associated with CO₂ transport would be very low. This is so because in an industrial-scale implementation of a mineral carbonation technology, the silicate feedstock would be carbonated in commercial facilities located adjacent to, or near, large “point sources” of CO₂ generation, such as fossil fuel-fired power plants and cement factories. In contrast, CO₂ sequestration in deep brine aquifers, or the benthic regions of the world’s major oceans, would generally require transport of liquid CO₂ over substantial distances. Building and maintaining many miles of pipeline to achieve such transport—or hauling liquid CO₂ over long distances by truck, train or ship—would be extremely expensive, and perhaps totally impractical.

Finally, the following additional advantages of mineral carbonation are noteworthy: (1) by technical necessity, mineral carbonation involves rapid conversion of CO₂ to solid carbonate(s), and (2) by virtue of creating one or more solid carbonate phases from a volatile phase rich in CO₂, carbonate crystallization automatically produces a large reduction in total volume. It has already been demonstrated by researchers at the Albany Research Center in Oregon⁽⁴⁾, and the Los Alamos National Laboratory in New Mexico⁽⁵⁾, that, with vigorous mechanical stirring, olivine and heat-pretreated serpentine can be quantitatively converted to magnesite (see

Reactions 1 and 2 above) in ~30 minutes at 155°C and 185 atm total pressure. Significantly, the latter environmental conditions are readily attained in modern industrial reactors. A large reduction in the total volume of the reactants (CO₂, plus one or more condensed phases, ± one or more “additives” and/or catalysts) is automatically achieved in mineral carbonation because the CO₂-bearing solids produced are >1000x more dense than gaseous CO₂ at STP (standard temperature and pressure—25°C, 1 atm). This contraction essentially eliminates the “room problem” associated with storing large volumes of CO₂ (as a gas, liquid or supercritical fluid) in subsurface rock formations.

While it is evident that mineral carbonation offers many important advantages over competing CO₂ sequestration technologies, it is also true that it suffers two major disadvantages. Chief among these is the need to mine, or quarry, large quantities of silicate feedstock to sequester the gigatons of atmospheric CO₂ generated annually by combustion of fossil fuels at power plants, and production of lime at cement factories. Excavating massive amounts of rock and soil to permit silicate carbonation at sites near major industrial sources of CO₂ will be expensive, and will require intense reclamation activities to restore the land to an environmentally acceptable state. However, there is no doubt that this can be accomplished using modern methods of environmental restoration. In addition, it is likely that new technologies will soon be developed to enable innovative synergies, and more satisfactory compromises, between large-scale energy production and traditional modes of land use.

The second major disadvantage of mineral carbonation is that elevated temperatures and pressures, and chemical “additives” and/or catalysts, are required to accelerate CO₂ conversion to one or more crystalline carbonates. While considerable success has already been achieved in carbonating olivine (Reaction 1) at commercially feasible temperatures and pressures⁽⁴⁾, mineral carbonation experiments performed over the past four years at the Albany Research Center have shown that *untreated* serpentine does not react as readily (Reaction 2). This is a serious problem because, while significant masses of olivine-bearing rocks exist around the world, naturally occurring serpentine is approximately an order of magnitude more abundant. To date, the only known remedy for sluggish serpentine carbonation is to heat-pretreat the mineral to 600-650°C prior to carbonation, which drives off structurally bound water (hydroxyl groups)⁽⁴⁾. Tests of this altered (dehydroxylated) serpentine have shown that it is much more reactive than untreated (hydroxylated) serpentine. However, at a typical fossil fuel-fired power plant, heat treating serpentine at 600-650°C prior to carbonation would require ~200 kW·hr of electricity per ton of serpentine feedstock⁽⁴⁾. With one ton of carbon in a fossil fuel producing ~3.7 tons of CO₂, and each ton of CO₂ consuming ~2.0 tons of serpentine during carbonation, the power requirements for serpentine dehydroxylation represent 20-30% of total power output. This large energy penalty threatens the economic viability of CO₂ sequestration by serpentine carbonation.

Faced with the difficulty that carbonation of hydroxylated serpentine by Reaction 2 is very sluggish, scientists at the Albany Research Center and the Los Alamos National Laboratory have been actively investigating potential alternative serpentine-carbonation pathways^(13,14). A major

goal of this work is to identify a pretreatment protocol that either reduces the temperature where serpentine dehydroxylates at 1 atm, or circumvents the need to heat-pretreat serpentine by inducing its decomposition chemically at STP. Unfortunately, to date these avenues of investigation have failed to produce any significant breakthroughs.

The current status of mineral carbonation R&D suggests an overemphasis on the use of magnesium silicates as a process feedstock. It is now generally accepted that olivine, by itself, is insufficiently abundant to support a wide-scale silicate carbonation technology. This leaves serpentine as the only feasible major source of the magnesium needed to produce large masses of magnesite. Recently, scientists at the Los Alamos National Laboratory studied the worldwide distribution of potentially mineable bodies of serpentine, and concluded that a sufficient number of deposits exist to sequester all of the anthropogenic CO₂ currently being generated⁽⁹⁾. However, their results also showed that large serpentine bodies are generally restricted to special geological regions of limited areal extent. For example, in the U.S., *large* bodies of serpentine are found only in North Carolina, California and Oregon. This is significant, because it suggests that a serpentine-based silicate carbonation technology might necessarily involve either (i) transporting serpentine long distances to major sites of energy and cement production, or (ii) locating electrical plants and cement factories close to the regional sources of serpentine. The former circumstance would greatly increase costs of silicate carbonation, and the latter strategy might prove to be impractical because, while costs of hauling serpentine would be sharply reduced, expenses associated with transport of electricity and cement to major population centers could be prohibitively high.

It is evident from Reactions 3 and 4 that the problems plaguing serpentine carbonation would be partly or entirely avoided if a more abundant silicate mineral could be utilized. In this regard, it is noteworthy that wollastonite is carbonated by Reaction 3 at 60°C using an aqueous solution of acetic acid as a catalyst⁽¹⁵⁾. This result is of some scientific interest, but it fails to significantly bolster silicate carbonation as a potential means for sequestering large masses of CO₂ because wollastonite, while not rare in nature, is typically found in significant quantities only in contact metamorphic aureoles where it tends—along with other silicates—to form small, isolated bodies adjacent to igneous intrusions. The other principal occurrence of wollastonite is as a widely disseminated mineral in regionally metamorphosed carbonate strata. Thus, wollastonite is not available in sufficient quantities to sustain a wide-scale silicate carbonation technology.

The foregoing analysis leaves plagioclase as the major potential source of calcium (Reaction 4) to produce the quantities of carbonate required to sequester gigatons of CO₂ by silicate carbonation. (Other, *locally* significant potential sources of calcium include Ca-rich clay deposits, Ca-rich fly ash, and waste concrete.) However, a commercially feasible plagioclase carbonation technology faces two formidable technical challenges. First, it is inherently difficult to extract calcium from plagioclase because, being a framework silicate with a three-dimensional structure held together by tightly bonded atoms of silicon and aluminum, plagioclase is not

readily destabilized by firing at high temperatures, or easily “digested” by customary solvents (HF and NaOH excepted). Second, while most plagioclases contain a significant amount of calcium, Ca-contents are always less than that of wollastonite. Therefore, per ton of silicate feedstock, less calcium-rich carbonate (calcite) is formed from plagioclase than from wollastonite. These difficulties notwithstanding, it is clear that plagioclase carbonation merits serious scientific study to determine whether it could be an attractive alternative to serpentine carbonation in sequestering large quantities of CO₂.

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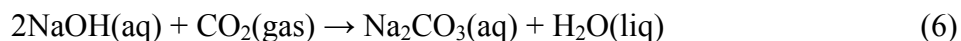
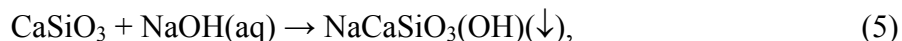
3. Detailed Description of the Invention

We have developed a three-step chemical process for producing calcite (CaCO₃) and carbonate-cancrinite [Na₈(AlSiO₄)₆CO₃·2H₂O] from calcium silicates and gaseous CO₂. The overall conversion reaction is

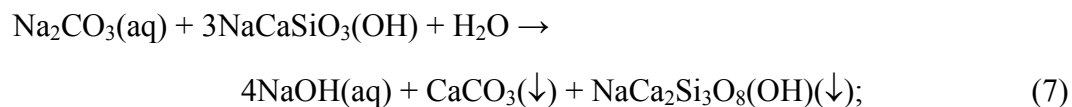


The steps in the process are: (1) "digestion" of the Ca-silicate in an aqueous solution of caustic soda (NaOH) to form crystalline portlandite [Ca(OH)₂] or crystalline sodium-calcium hydroxysilicate [NaCaSiO₃(OH)] ± crystalline hydroxy-sodalite [Na₈(AlSiO₄)₆(OH)₂]—followed by physical and chemical segregation of the precipitated solid(s) and "depleted" caustic liquid; (2) reaction of CO₂ (either pure CO₂ or CO₂-bearing flue gas) with caustic soda (aqueous NaOH) to produce aqueous ± crystalline sodium carbonate (Na₂CO₃) + water (H₂O); and (3) reaction of the aqueous ± crystalline sodium carbonate generated in step 2 with the crystalline portlandite or crystalline sodium-calcium hydroxysilicate ± crystalline hydroxy-sodalite created in step 1 to produce calcite ± carbonate-cancrinite + caustic soda. Each of the reactions in these three steps has been verified by autoclave experiments performed at 200°C and pressures <15 atm for periods ranging from ~1 hour to 3 days using natural wollastonite (CaSiO₃), anorthite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x})O₈, where x ≥ 0.9], labradorite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x})O₈, where 0.5 ≤ x ≤

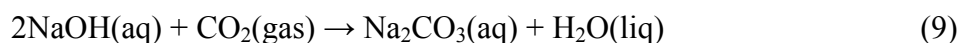
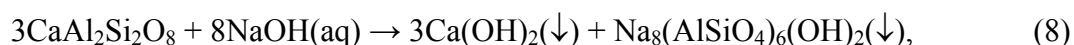
0.7], Ca-rich fly ash, and basalt (a volcanic rock rich in Ca, Mg and Fe) as model Ca-silicate feedstocks (Table 1). For wollastonite and anorthite, the processing reactions are:



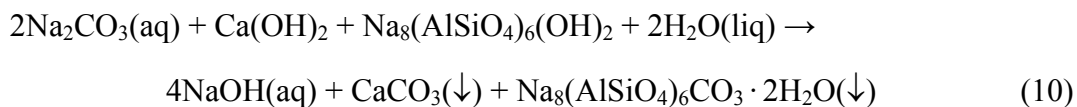
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(aq = aqueous, ↓ = precipitate, liq = liquid), respectively. (Other Ca-rich aluminosilicates carbonate by reactions similar to those for anorthite.) The NaOH “regenerated” in step 3 of the process is recycled to form additional Na₂CO₃ in step 2.

4. Related Technologies

Our new silicate carbonation process is analogous to, but distinctly different from, the commercial chemical processes that are used to extract alumina (Al₂O₃) from bauxite (aluminum ore), and to generate caustic soda from trona (a rock rich in sodium carbonate, Na₂CO₃).

In the treatment of bauxite ore by the well-known Bayer Process, caustic soda is used to remove reactive silica and iron oxides, and to dissolve aluminum oxides (gibbsite, boehmite and diasporite). Currently, bauxites containing greater than seven percent reactive silica cannot be economically processed. Dissolution of silica by the caustic solution produces sodium silicate (nominally Na₂SiO₃), which quickly reacts with sodium aluminate (NaAlO₂) to form crystalline hydroxy-sodalite [Na₈(AlSiO₄)₆(OH)₂]. This desilication of the solution is detrimental to the overall process because it consumes caustic, and the total mass of dissolved sodium aluminate is lowered. (With less sodium aluminate in solution, less high-purity gibbsite is precipitated in a later stage of the process, and as a second consequence, less caustic soda is regenerated by gibbsite precipitation. Regenerated caustic soda is recycled in the Bayer Process to treat additional batches of bauxite ore.)

While the Bayer Process has several characteristics in common with the process described in this document—in particular, the use of caustic soda to “digest” the silicate feedstock, and

regeneration of caustic soda at a subsequent stage of the process—two major differences are also evident. The first is that the goals of the two processes are totally different: the Bayer Process was developed to produce a solid concentrate rich in aluminum (precipitated gibbsite), whereas the principal intent of our silicate carbonation process is to form stable carbonate compounds for long-term CO₂ sequestration. Due to this key difference, the “ore” used for the two processes is much different. In the Bayer Process, deeply weathered, unconsolidated rock material is reacted because it is rich in alumina and poor in silica. In our process, the silica content of the Ca-silicate feedstock is not a significant factor—except that a greater silica content generally means a lower calcium content, which is undesirable. The second key difference between our three-step silicate carbonation process and the Bayer Process is that, in our process, caustic soda is regenerated by reacting sodium carbonate with portlandite or sodium-calcium hydroxysilicate ± hydroxy-sodalite, whereas in the Bayer Process, caustic soda is regenerated during the production of high-purity gibbsite.

The second commercial process that bears some similarity to our silicate carbonation process is the reaction of trona with lime (CaO) to produce caustic soda plus calcite. This transformation is similar to that accomplished in step 3 of our process in that caustic soda and calcite are produced, but two critically important differences should be noted. First, the intent of reacting trona with lime is solely to produce caustic soda; the entire amount of calcite formed as a byproduct is subsequently calcined to regenerate lime, which is recycled for reaction with additional batches of trona ore to produce more caustic soda. Thus, there is no CO₂ sequestration achieved in the commercial treatment of trona. Second, trona contains little or no silica and alumina; consequently, its treatment to generate caustic soda does not consume or produce any significant amount of silicate or aluminosilicate material.

5. Unique Features

Our new Ca-silicate carbonation process has two, critically important unique features compared to competing silicate carbonation processes developed by previous investigators. First, by using a concentrated aqueous solution of caustic soda (NaOH) as the silicate solvent in the first step of the process, we have demonstrated, for the first time, by documented autoclave experimentation (Table 1), that a wide variety of calcium silicates—viz., wollastonite (CaSiO₃), anorthite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O₈, where $x \geq 0.9$], labradorite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O₈, where $0.5 \leq x \leq 0.7$], and calcium-rich fly ash—can be rapidly converted to crystalline portlandite [Ca(OH)₂] or crystalline sodium-calcium hydroxysilicate [NaCaSiO₃(OH)] ± crystalline hydroxy-sodalite [Na₈(AlSiO₄)₆(OH)₂] at 200°C, with total (fluid) pressure <15 atm. Second, by using aqueous ± crystalline sodium carbonate (Na₂CO₃) as a source of CO₂ in the third step of our process, we have proven, by documented autoclave experimentation (Table 1), that, at 200°C and total pressures <15 atm: (i) crystalline portlandite and crystalline sodium-calcium hydroxysilicate are readily transformed to crystalline calcite (CaCO₃), (ii) crystalline hydroxy-

sodalite is readily converted to crystalline carbonate-cancrinite $[\text{Na}_8(\text{AlSiO}_4)_6\text{CO}_3 \cdot 2\text{H}_2\text{O}]$, and (iii) caustic soda is generated as calcite and carbonate-cancrinite crystallize.

6. Possible Alternative Versions

The scope of our process encompasses the following modifications of its general characteristics.

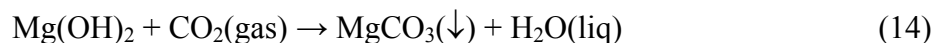
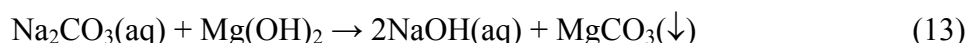
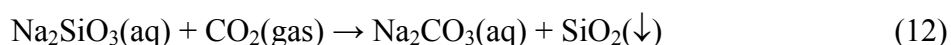
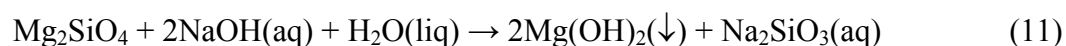
1. Reaction temperature at each step of the process could be either higher or lower than 200°C. Our proof-of-principle experiments have demonstrated the technical feasibility of the process at 200°C (Table 1), but it is likely that a reaction temperature greater or less than 200°C would yield similar or superior results in equal or shorter periods of time. Optimization of the process might also reveal that the best overall results are obtained with different reaction temperatures at each step of the process.
2. Total pressure in step 3 of the process could be higher than that reached in our proof-of-principle experiments (<15 atm). Our autoclave experiments with Ca-rich silicates (Table 1) were performed at 200°C, with total pressure equal to (established by) the vapor pressure of the liquid phase. Since the vapor pressure of pure water is slightly greater than 15 atm at 200°C, the three liquid compositions created in our process—concentrated aqueous solutions of NaOH (step 1), Na_2CO_3 (step 2), and $\text{Na}_2\text{CO}_3 + \text{NaOH}$ (step 3)—will have vapor pressures less than 15 atm, because dissolution of NaOH and Na_2CO_3 reduces water activity. Achieving rapid chemical reaction at these very low total pressures is a key advantage of our process, because relatively thin-walled pressure chambers will suffice to safely contain the fluids as they flow through the carbonation reactor, thereby reducing construction costs. Moreover, no investments in expensive pressure-intensifying equipment are necessary. On the other hand, higher fluid (“headspace”) pressures at each step might lead to more rapid and efficient chemical reaction, and if this is borne out by further testing, then additional capital expenditures to make the carbonation reactor more structurally robust, and to procure suitable pumping equipment, might be cost effective. In step 1 of the process, a higher total pressure could be achieved by forcefully injecting nitrogen into the headspace above the caustic liquid present at that stage. However, an elevated headspace pressure is much more likely to be beneficial in step 2 of the process, because the gas injected into the reactor at that stage would be flue gas or pure CO_2 , either of which—at an elevated pressure—could prove to be effective in increasing the carbonation rate of sodium hydroxide. Finally, if CO_2 is captured, separated and liquified by a process other than the one described in this document, then pressures between 1 atm and ~64 atm (the vapor pressure of pure liquid CO_2 at 25°C) could be achieved simply by throttling gas flow into the pressure chamber used to carbonate sodium hydroxide in step 2 our process.

3. The concentration of NaOH in the caustic solution used in step 1 of the process was chosen arbitrarily. In the autoclave experiments we performed to investigate the reactions that occur in step 1 of the process, the starting caustic solution was a 50:50 weight percent mixture of NaOH and H₂O. This composition was selected because it is widely available commercially. However, future optimization experiments may indicate that superior results are obtained using a more concentrated, or a more dilute, caustic solution.
4. Many different types of Ca-silicate feedstocks are amenable to carbonation by our process. We have shown, by documented autoclave experimentation (Table 1), that wollastonite (CaSiO₃), anorthite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O₈, where $x \geq 0.9$], labradorite [(Ca_x,Na_{1-x})(Al_{1+x}Si_{3-x}O₈, where $0.5 \leq x \leq 0.7$], calcium-rich fly ash, and basalt (a volcanic rock rich in Ca, Mg and Fe) are readily carbonated at 200°C and total pressures < 15 atm. Ca-rich montmorillonite [nominally (½Ca,Na)_{0.7}(Al,Mg,Fe)₄[(Si,Al)₈O₂₀](OH)₄·nH₂O] and waste concrete are two additional potentially suitable feedstocks for our process.
5. The average grain size of the Ca-silicate feedstock, the extent to which liquids are agitated or stirred, and control of the proportions of phases as reaction proceeds, are all key variables in our process. It is generally observed in chemical processes that reactions among gases, liquids and solids are accelerated by: fine grinding the solid(s), vigorously agitating or rapidly stirring the reactants as processing proceeds, and maintaining high fluid (liquid or gas)/solid ratios. In the autoclave experiments performed to validate our process, solid starting materials were ground to an average grain size less than 10 microns using a Siebtechnik shatterbox, and during experimentation each liquid/solid “slurry” was gently stirred by a Teflon-coated bar magnet magnetically coupled to an external, motor-driven shaft/horseshoe magnet assembly rotating at 120 rpm. Moreover, excess amounts of sodium hydroxide and sodium carbonate were added to samples reacted to investigate chemical transformations in our process, because the main goal of that work was to detect chemical reaction, not optimize it. Thus, reaction rates faster than those observed in our experiments could probably be achieved by finer grinding of the Ca-silicate starting materials, more vigorous mechanical agitation/stirring of liquids, and/or increasing fluid/solid ratios. Clearly, the scope of our process includes a wide range of: (i) possible initial grain sizes for Ca-silicate starting materials, (ii) degrees to which the reactants are agitated or stirred during processing, and (iii) mass ratios of reacting phases at each step.
6. It is probably possible to precipitate calcite ± carbonate-cancrinite continuously as CO₂ (± N₂) is injected into the caustic solvent. Using a concentrated aqueous solution of caustic soda (50 weight percent NaOH in H₂O) as the silicate solvent, and by adding abundant sodium carbonate to that solution to serve as a source of CO₂, we have shown, by documented autoclave experimentation (Table 1), that the aluminum-bearing calcium

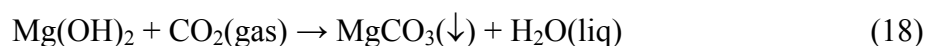
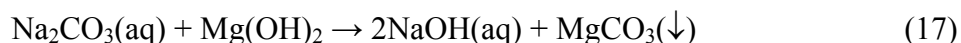
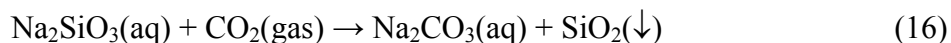
silicates anorthite $[(Ca_x, Na_{1-x})(Al_{1+x}Si_{3-x}O_8]$, where $x \geq 0.9$], labradorite $[(Ca_x, Na_{1-x})(Al_{1+x}Si_{3-x}O_8]$, where $0.5 \leq x \leq 0.7$], and calcium-rich fly ash react with NaOH and Na_2CO_3 to form crystalline calcite \pm sodium-calcium hydroxysilicate \pm crystalline sodalite \pm aluminosilicate material at 200°C and a total (fluid) pressure <15 atm. Therefore, we have shown that various Ca-rich silicates can be carbonated to a significant extent in a *single-step* process that is very similar to the three-step process that we have described in this document.

The single-step process for carbonating Ca-rich silicates described above should be regarded as a variant of our three-step process. It is intrinsically simpler, because physical and chemical segregation of the solid and liquid products of caustic digestion is not required as is the case in the three-step process. However, the one-step process has the serious disadvantage that carbonate-cancrinite is generally not among the solids that form. (In our experiments, carbonate-cancrinite was only observed in one-step carbonation experiments performed with Ca-rich fly ash.) A plausible explanation for this is that the aqueous fluids produced in our one-step experiments were usually too basic to allow carbonate-cancrinite to crystallize. This result is important, because the formation of carbonate-cancrinite significantly increases the total “CO₂-loading” of the solids produced, and therefore leads to more efficient and cost-effective carbonation of the Ca-silicate feedstock.

7. Our process also converts magnesium-rich silicates to magnesium-rich carbonates. The following reactions produce magnesite (MgCO₃) from the magnesium-rich minerals olivine (Mg₂SiO₄) and serpentine [Mg₃Si₂O₅(OH)₄]:



[Net reaction: $Mg_2SiO_4 + 2CO_2(gas) \rightarrow 2MgCO_3(\downarrow) + SiO_2(\downarrow)$], and

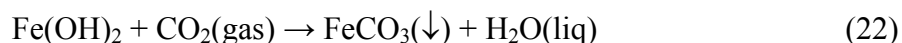
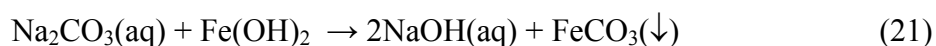
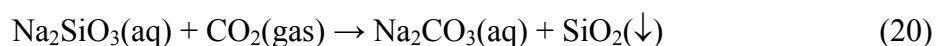
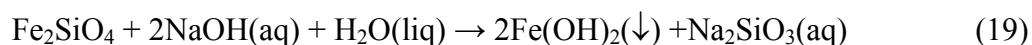


[Net reaction: $Mg_3Si_2O_5(OH)_4 + 3CO_2(gas) \rightarrow 3MgCO_3(\downarrow) + 2SiO_2(\downarrow) + 2H_2O(liq)$].

Significantly, all of these reactions, with the notable exception of formation of NaOH and

MgCO₃ from Na₂CO₃ and Mg(OH)₂, have been verified by preliminary experiments we have performed at 200°C (Table 2). Concerning experiments performed with aqueous Na₂CO₃ and crystalline Mg(OH)₂ as starting materials, two distinctly different results were obtained. First, no reaction was observed when total (fluid) pressure was equal to the vapor pressure of the Na₂CO₃-H₂O liquid phase (<15 atm). This is unfortunate, because reaction of Na₂CO₃ and Mg(OH)₂ to form NaOH and MgCO₃ in step 3 of our process would greatly lower the costs of carbonating olivine and serpentine. On the other hand, it was also observed in our experiments (Table 2) that raising CO₂ fugacity to 60-65 atm at 200°C caused Na₂CO₃ to react with Mg(OH)₂ to form the double carbonate eitelite [Na₂Mg(CO₃)₂], which contains twice as much CO₂ as magnesite (MgCO₃). This is a key result because, compared to magnesite, crystallization of eitelite would permit twice as much CO₂ to be sequestered per ton of mined Mg-rich rock. In addition, like magnesite, eitelite is thermodynamically stable, environmentally neutral, and only weakly soluble in meteoric water. Concerning reaction of Na₂CO₃ with Mg(OH)₂ to form NaOH and MgCO₃, we conclude that a special combination of the key variables in step 3 of our process—temperature, total pressure, CO₂ fugacity, liquid composition, and/or liquid pH—are required to allow NaOH + MgCO₃ to form.

8. Our chemical process may also convert iron-rich silicates to iron-rich carbonates. In principle, carbonation pathways similar to those we have already developed for Ca- and Mg-rich silicates will convert iron-rich silicates to iron-rich carbonates. This is illustrated below for the iron-rich mineral fayalite, Fe₂SiO₄:



[Net reaction: Fe₂SiO₄ + 2CO₂ → 2FeCO₃ + SiO₂]. This and similar carbonation pathways for iron silicates, including Fe-bearing silicate glasses (e.g., basaltic glass), are to be regarded as variants of the carbonation pathways we have already developed for Ca- and Mg-rich silicates.

7. Probable Uses

Commercial application of our new silicate-carbonation process depends heavily on world economies becoming “carbon-constrained” sometime in the future. This might involve, for example, the creation of carbon credits—or some form of globally instituted taxation—to reduce industrial CO₂ emissions to the atmosphere. In such a circumstance, our process would have the following practical uses and side benefits.

- CO₂ sequestration. Our process was designed to produce crystalline carbonates that persist indefinitely in most continental habitats. Toward that end, we have demonstrated—by documented autoclave experimentation (Tables 1 and 2)—that: Ca-rich silicates are readily converted to calcite (CaCO₃) and carbonate-cancrinite [Na₈(AlSiO₄)₆CO₃·2H₂O], and Mg-rich silicates are quickly transformed to magnesite (MgCO₃) and eitelite [Na₂Mg(CO₃)₂]. These four carbonate compounds bind CO₂ indefinitely in non-acidic terrestrial environments, and are completely harmless to all flora and fauna.
- Neutralization of highly acidic soils. Locally, calcium and magnesium carbonates can have commercial value as soil amendments. While adding carbonates to highly acid soils to increase pH ultimately releases CO₂ to the atmosphere, significant environmental and economic benefits would accrue if the treated land was made more biologically productive. The amended soils might be used to grow crops or trees, either of which could have a total carbon sequestration potential higher than that of the crystalline carbonate amendment. Using calcium and magnesium carbonates for this purpose would also lessen demand for lime produced by calcining limestone, and this would help lower CO₂ emissions to the atmosphere.
- Recovery of useful metals. Many rock formations contain useful metals (e.g., iron, copper, nickel and platinum) at concentrations that are currently uneconomical to mine. If, however, mining and grinding were already being performed to create a silicate feedstock for mineral carbonation, the metals might be extracted as a byproduct, thereby reducing the costs of mineral carbonation.
- Elimination of hazardous mine tailings. Mine tailings, consisting of crushed rock material from which metals or other elements of interest have been extracted—along with the “overburden” (soil and regolith) that is removed to access buried ore horizons—are an important waste problem for many active and abandoned mines. Thus, it is significant that a nearby mineral carbonation reactor might be able to use them as a source of calcium and magnesium. This would enhance environmental restoration, and reduce the costs of mining silicate feedstock for mineral carbonation.
- Production of high-purity silica. When either olivine or serpentine is carbonated by our process, the solid effluent produced in step 2 is high-purity silica, which can be refined

for use in manufacturing silica-based desiccants, silica brick, silicon carbide, and various types of glass. High purity silica is also a potential source of elemental silicon—the foundation material for numerous semiconducting electronic devices. Finally, it may be possible to use amorphous silica to form melanophlogite, a silica-rich compound with a cage structure that can accommodate as many as six CO₂ “guest” molecules for every 46 molecules of SiO₂. Creation of substantial amounts of melanophlogite would significantly increase the total CO₂-loading of the solids generated by our process.

- Capture and separation of CO₂ from flue gas. Another, quite different, potential application of our process is especially important, as it would greatly reduce costs associated with capture and separation of CO₂ at fossil fuel-fired power plants. Specifically, step 2 in our process permits CO₂ to be captured and separated from flue gas by bubbling the gas through a NaOH- or Na₂SiO₃-bearing aqueous liquid. The CO₂ would be transformed to aqueous ± crystalline Na₂CO₃ (Reactions 6, 9, 12 and 16), and the nitrogen-rich gas effluent could either be refined to produce high-purity nitrogen for industrial use, or simply released harmlessly to the atmosphere.

8. Specific Contribution to the Concept of the Invention

Dr. James G. Blencoe developed the general framework of the process, and recognized how it might be used in a commercially viable, pollution-free technology for capturing, separating and sequestering large masses of CO₂ created by energy and cement production. After Dr. Anovitz discovered that numerous magnesium and calcium silicates are readily transformed to solid hydroxides (plus various silicate and/or aluminosilicate byproducts) by reaction with a 50 weight percent aqueous solution of caustic soda at 200°C and a total (fluid) pressure <15 atm, Dr. Blencoe discerned the need to investigate the possibility that formation of thermodynamically stable, environmentally neutral, and sparingly soluble crystalline carbonates could be achieved by reacting the solid Mg- and Ca-hydroxides with sodium carbonate—the latter being formed by the reactions $2\text{NaOH}(\text{aq}) + \text{CO}_2(\text{gas}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{liq})$ and $\text{Na}_2\text{SiO}_3(\text{aq}) + \text{CO}_2(\text{gas}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{SiO}_2(\downarrow)$. Blencoe was also the first to discover that the new process has several important characteristics in common with commercial chemical processes that are employed to extract alumina from bauxite (aluminum ore), and to generate caustic soda from trona (a natural rock rich in sodium carbonate).

Dr. Lawrence M. Anovitz made the crucially important discovery that numerous magnesium and calcium silicates react to crystalline hydroxides in the presence of a 50 weight percent solution of caustic soda at 200°C and a total pressure (<15 atm) established by the vapor pressure of the caustic fluid.

Dr. Donald A. Palmer provided important insights on the chemical reactions that occur in the process. His extensive knowledge of speciation and equilibria in aqueous fluids was particularly helpful in planning experiments and assessing experimental results.

Dr. James S. Beard contributed to development of the process by recognizing that, in many respects, it is analogous to the natural geochemical processes that operate during the formation of calcite, brucite and magnesite in seafloor hydrothermal systems. Dr. Beard contended from the outset that valuable indirect information on mineral carbonation (e.g., the temperatures, pressures and pHs at which calcium and magnesium silicates carbonate most rapidly) could be gleaned from studies of natural settings in which rocks have reacted with CO₂-bearing gases and hydrothermal fluids at elevated temperatures and pressures.