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A METHOD FOR PERMANENT CO_2 SEQUESTRATION: SUPERCRITICAL CO_2 MINERAL CARBONATION

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Abstract

The Albany Research Center (ARC) of the U.S. Department of Energy (DOE) has been conducting research to investigate the feasibility of mineral carbonation as a method for carbon dioxide (CO_2) sequestration. The research is part of a Mineral Carbonation Study Program within the Office of Fossil Energy in DOE. Other participants in this Program include DOE's Los Alamos National Laboratory and National Energy Technology Laboratory, Arizona State University, and Science Applications International Corporation.

The research has focused on ex-situ mineral carbonation in an aqueous system. The process developed at ARC reacts a slurry of magnesium silicate mineral with supercritical CO_2 to produce a solid magnesium carbonate product. To date, olivine and serpentine have been used as the mineral reactant, but other magnesium silicates could be used as well. The process is designed to simulate the natural serpentinization reaction of ultramafic minerals, and consequently, these results may also be applicable to strategies for in-situ geological sequestration.

Baseline tests were begun in distilled water on ground products of foundry-grade olivine. Tests conducted at 150° C and subcritical CO_2 pressures (50 atm) resulted in very slow conversion to carbonate. Increasing the partial pressure of CO_2 to supercritical (>73 atm) conditions, coupled with agitation of the slurry and gas dispersion within the water column, resulted in significant improvement in the extent of reaction in much shorter reaction times. A change from distilled water to a bicarbonate/salt solution further improved the rate and extent of reaction.

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When serpentine, a hydrated mineral, was used instead of olivine, extent of reaction was poor until heat treatment was included prior to the carbonation reaction. Removal of the chemically bound water resulted in conversion to carbonate similar to those obtained with olivine. Recent results have shown that conversions of nearly 80 pct are achievable after 30 minutes at test conditions of 155° C and 185 atm CO_2 in a bicarbonate/salt solution.

The results from the current studies suggest that reaction kinetics can be further improved. Future tests will examine additional pressure/temperature regimes, various pretreatment options, and solution modifications.

Introduction

The international community has become increasingly concerned that greenhouse gas emissions have a potentially adverse effect on global climate conditions. Carbon dioxide (CO_2) is considered the most significant of the greenhouse gases, and reduction of CO_2 emissions from the energy and process industries has become increasingly emphasized as a primary environmental concern. Reductions can be achieved by efficiency improvements in fossil-fuel-fired power plants, use of alternative energy technologies, sequestration of CO_2, energy conservation, and combinations of these methods. The availability of fossil-fuel resources ensures that they will continue to play a significant role in the world's energy economy well into the future. Thus, emphasis must be placed on improving the efficiency of fossil-fuel-fired power plants, as well as on methods to sequester the CO_2 emitted from these plants.

The U.S. Department of Energy (DOE) has identified technological opportunities in energy efficiency, clean energy, and carbon sequestration and management to reduce greenhouse gas emissions (National Laboratory Directors, 1997). Herzog, et al. (1997), summarized CO_2 capture, reuse, and storage technologies, and proposed an initial research plan to address CO_2 emissions abatement strategies.

Sequestration may take many forms. Forestation and biomass utilization remove CO_2 from the atmosphere by botanical and biological activity. Terrestrial storage of CO_2 is possible in depleted oil or gas wells and unmineable coal seams Aquifer storage involves injection of CO_2 into deep brine formations where it is trapped hydrodynamically. Deep-sea storage would place CO_2 into the ocean below approximately 3,000 meter depths where it would theoretically form stable pools of liquid CO_2. In mineral carbonation, CO_2 reacts with minerals to form solid, environmentally benign carbonate minerals. This last form of sequestration is a permanent method, because the mineral carbonates are stable over geologic time periods (millions of years), rather than the hundreds to thousands of years of stability expected for the first three forms of sequestration.

Lackner, et al. (1997), proposed CO_2 storage as mineral carbonates with an aqueous process that uses hydrochloric acid (HCl) to leach serpentine and produce magnesium chloride ($MgCl_2$). This reaction was investigated by the Tennessee Valley Authority and U.S. Bureau of Mines during World War II as an alternative process for the production of magnesium metal (Houston, 1944; Gee, 1946). However, the complexity of the carbonation process led researchers at DOE's Albany Research Center (ARC, Albany, Oregon) to consider direct carbonation with carbonic acid as an alternative mineral-carbonation process. DOE has filed a report of invention for the direct carbonic-acid process (O'Connor, et al., 1999a). The research is part of a Mineral Carbonation Study Program within the Office of Fossil Energy in DOE. Other participants in this Program include DOE's Los Alamos National Laboratory and National Energy Technology Laboratory, Arizona State University, and Science Applications International Corporation.

In the direct carbonic-acid process, CO_2 is dissolved in a slurry of water (or aqueous solution) and magnesium-silicate mineral reactant, such as forsterite (Mg_2SiO_4) or serpentine [$Mg_3Si_2O_5(OH)_4$]. The CO_2 reacts with water to form carbonic acid (H_2CO_3), which dissociates to H^+ and HCO_3^-. Reaction of the carbonic acid with the mineral consumes the H^+ and liberates Mg^{2+} cations that react with the bicarbonate (HCO_3^-) to form the solid carbonate mineral, magnesite ($MgCO_3$). Because the slurry is under high partial pressure of CO_2 (P_{CO2}), the carbonic acid is continuously regenerated as it is consumed, and the reaction sequence is maintained until the mineral reactant is exhausted. The theorized reaction is described by the following equation:

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4 \, [\textit{or } SiO_2 + 2H_2O] \qquad (1)$$

The direct carbonic-acid method dramatically simplifies the mineral-carbonation process flowsheet, because the mineral-dissolution and mineral-carbonation reactions are combined in a single unit operation.

The tonnage of mineral reactant necessary for any ex-situ process is significant. A single 500-MW power plant generates approximately 10,000 tons CO_2/day and would require about 23,000 tons/day of magnesium silicate ore. The estimate assumes a mean magnesium oxide (MgO) content of 40 pct in the magnesium silicate ore mineral (all analyses in this paper are based on weight), 80 pct efficiency of the carbonation reaction, and the stoichiometry of equation 1.

Several magnesium silicate minerals are suitable for the carbonation reaction described above, including serpentine [$Mg_3Si_2O_5(OH)_4$], enstatite ($MgSiO_3$), and olivine, a mineral group comprising the solid-solution series with magnesium-rich forsterite (Mg_2SiO_4) and iron-rich fayalite (Fe_2SiO_4) as end members. These minerals occur geologically in ultramafic complexes, several of which in North America contain sufficient quantities of magnesium silicate minerals to provide raw materials for the mineral carbonation of U.S. power-plant CO_2 emissions for many years (Goff, et al., 1997). Serpentine is an alteration product of olivine and other magnesium silicates, and occurs in huge deposits on both the east and west coasts of North America. Olivine, particularly the forsterite end member, is also found in huge deposits on both coasts (Hunter, 1941; IGCP, 1977), although not to the extent of serpentine.

The scale of proposed operations for any ex-situ mineral carbonation process leads to concerns of economic and environmental impacts. The research conducted at ARC is intended to provide an understanding of the reaction mechanics and meaningful engineering data to estimate the costs of an industrial process.

Experimental

Materials

In the initial tests of the investigation, simplification of the reaction sequence was desired. A foundry-grade olivine sand was selected, because it was a high-purity magnesium silicate mineral with a high MgO concentration. Following a series of carbonation tests with olivine, during which basic reaction parameters were established, serpentine was included in the study. Serpentine is a hydrated magnesium silicate mineral that is structurally more complex than olivine, and it contains a lower molar concentration of MgO.

The chemical compositions and x-ray diffraction (XRD) data for the olivine and serpentine samples used for the tests to date are summarized by O'Connor, et al (2000a). The analyses for the serpentine used in tests described in this report are included in table 1.

Table 1. Chemical composition of the serpentine head and typical heat-treated serpentine feeds, pct.

Oxide	Head	Heat-treated in air	Heat-treated in CO_2
Al_2O_3	0.17	0.20	0.27
CaO	0.08	0.09	0.15
FeO	3.50	0.85	3.40
Fe_2O_3	3.27	7.31	4.55
MgO	40.6	48.1	45.4
K_2O	0.003	0.005	0.004
SiO_2	36.2	40.4	40.4
Na_2O	0.01	0.006	0.01
Volatiles			
CO_2	0.46	0.24	0.29
C, fixed	0.02	0.01	<0.01
H_2O, dehyd.[1]	0.31	0.75	0.68
H_2O, bonded[2]	13.6	3.59	3.22
Total	98.2	101.6	98.4

[1] Water of dehydration (free moisture): weight loss measured after 1 hour at 105° C in air.

[2] Chemically-bonded (interstitial) water, measured as the difference between LOI and all other volatiles. LOI (Loss on Ignition): weight loss measured after 1 hour at 1,000° C in argon.

The MgO concentration is of most interest: the foundry-grade olivine used in the initial tests contained 49.7 pct MgO, and the serpentine used in these tests contained 40.6 pct MgO. Like olivine, serpentine represents a mineral group that includes antigorite, chrysotile, and lizardite; the serpentine used in these tests was primarily antigorite. The presence of chrysotile, the asbestiform variety of serpentine, would likely require additional safety considerations during mining and milling to minimize air-borne contamination. Chrysotile has not been identified in the carbonation reaction products.

Methods

The initial proof-of-concept tests were conducted with 5-g samples in 20 ml of distilled water in 45-ml stainless steel autoclaves in an oil bath to maintain temperature and magnetic stir bars for agitation. The tests were then scaled up to use 100 g of solids in 400 ml distilled water in a 2-liter (L) autoclave with agitation (stirring), and process parameters were monitored and recorded continuously. Details of the early procedures are described by O'Connor, et al. (1999b).

After a number of tests in the 2-L autoclave, a new system was assembled with a similar 2-L autoclave that included a gas-dispersion impeller on the stirring shaft, improved data collection, and a CO_2 gas booster pump controlled by a pressure switch. The inclusion of the gas booster pump permits operation under nearly constant P_{CO2}, which was not possible in the earlier test apparatus, due to consumption of CO_2 (and, thus, loss of pressure) in the reaction and/or to small leaks that resulted in loss of pressure over the extended times of the early tests.

In the test procedure as currently practiced, a slurry of 167 g of mineral ground to minus 37 microns (µm) and 950 ml of solution (15 pct solids) is sealed in the autoclave. The autoclave is purged with CO_2, and the slurry is stirred to keep it suspended during heating. After the slurry is heated to the desired temperature, the stirrer speed is raised to 2,000 rpm to ensure good gas dispersion, and CO_2 is injected to the desired operating pressure; water vapor pressure is calculated and counted in the total system pressure. The system is then held at the test conditions for the prescribed period of time; test times in this report do not include the time to heat and pressurize the system to the test conditions. At the conclusion of the test, the system is vented, and the carbonated slurry is then drained from the autoclave and filtered in a pressure filter to separate solids from the solution. The dried solids are weighed, the volume of filtrate is recorded, and samples of the solids and liquid are submitted for chemical analysis. The weight gain calculated from the dry weight of the residual solids provides a good estimate of the extent of the carbonation reaction, but the extents of reaction reported in this report are based on calculations with the chemical analyses of the solids before and after carbonation.

The initial tests conducted on serpentine produced much poorer carbonation results than those achieved with olivine under identical conditions. It was suspected that the more complex structure of the serpentine with its chemically bonded water was at least partially the reason for the poor results, so heat treatment of the serpentine was investigated as a pretreatment prior to the carbonation step. Initial tests were conducted in a tube furnace, either in air or in CO_2, under static, shallow-bed conditions. Recent tests have included periodic rabbling of the bed to improve removal of the water released from the mineral structure.

Results and Discussion

The results of early tests of the direct-carbonic acid process are summarized by O'Connor, et al. (2000a, 2000b). As the research has progressed, extents of reaction have increased or have been maintained as times required to achieve a level of carbonation have decreased. This paper describes results of a number of tests on serpentine carbonated for 3 hours or less. Table 2 shows tests in which the extent of reaction exceeded 75 pct in 1 hour or less.

Table 2. Carbonation tests on serpentine in which more than 75 pct conversion was achieved in 1 hour or less.

	Heat treatment			Carbonation			Stoichiometric
Test	atmosphere	temp, ° C	wt loss, pct	time, h	temp, ° C	P_{CO2}, atm	conversion, pct
SC-83	CO_2	650	12.6	1	155	150	82
SC-84	CO_2	650	12.6	0.5	155	185	78
SC-97	CO_2	800	13.8	1	155	150	82
SC-99[1]	CO_2	640	13.0	1	155	150	79
SC-100[1]	air	640	13.6	1	155	150	79
SC-102[1]	CO_2	1000	14.1	1	155	150	82

Particle size: minus 37 µm for all tests.
Carbonation starting solution: 0.64M $NaHCO_3$/1M NaCl.
[1] Nonmagnetic fraction from magnetic separation of serpentine.

Serpentine Pretreatment

Early tests on serpentine showed that heat treatment is necessary for successful carbonation, and minimization of oxidation of non-silicate iron (primarily magnetite) during heat treatment appears to be important. Most of the tests described in this report included a heat treatment conducted for 2 hours at approximately 650° C in a CO_2 atmosphere, resulting in consistent weight losses of about 11-13 pct. The loss-on-ignition (LOI) in argon at 1000° C of the heat-treated solids prior to carbonation is a measure of residual chemically bonded water. Low LOI (high weight loss) in the heat-treated serpentine feed is an important parameter in the subsequent carbonation reaction.

Differential thermal analysis and thermal gravimetric analysis of the serpentine show temperatures at which water is driven out of the serpentine structure (figure 1). Based on this analysis, a series of tests was conducted in which the heat-treatment temperature was varied. Weight loss ranged from less than 2 pct at 200° C to 14 pct at 1000° C. The effect of heat-treatment temperature (in CO_2 atmosphere) on the subsequent extent of carbonation is shown in figure 2. Heat treatment at 650° C results in a dramatic increase in the extent of reaction, but higher temperatures do not significantly improve results.

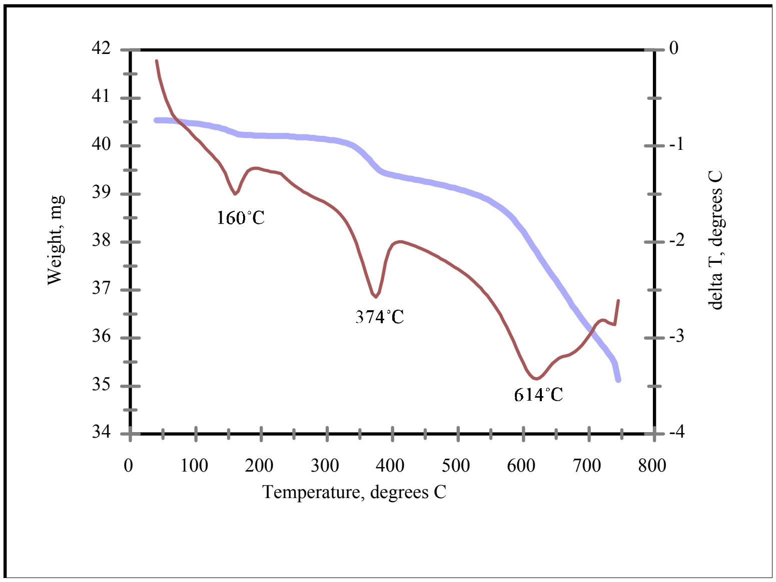

Figure 1. Differential thermal analysis (light line, right scale) and thermal gravimetric analysis (heavy line, left scale) of serpentine. Temperatures at which water is driven out of the mineral structure are shown.

<u>Solution chemistry</u>

Solution chemistry and pH have a large impact on the extent of reaction. Results were dramatically improved when a bicarbonate/salt solution was used instead of distilled water. In a series of tests that examined the effect of pH and ion species, several solutions were examined (figure 3). Acid systems and highly alkaline systems provided poor results. Both sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl) contribute to the reaction; results are improved with higher bicarbonate (HCO_3^{-2}) concentration (figure 4). The maximum concentration of $NaHCO_3$ achieved in a 1M NaCl solution at ambient temperature was 0.64 mole/L; the higher concentration (1.2M $NaHCO_3$/1M NaCl) was prepared at 50° C.

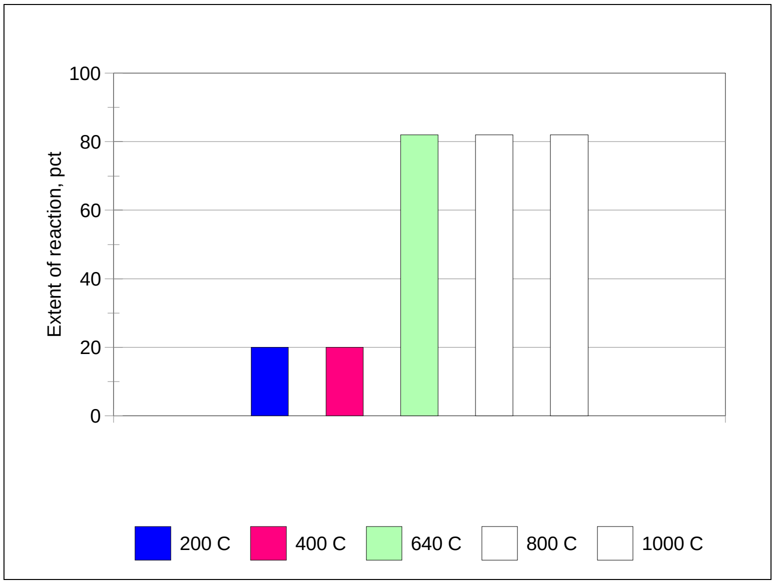

Figure 2. Effect of heat-treatment temperature on the extent of reaction. Tests were conducted for 1 hr at 155° C and 150 atm P_{CO2} in 0.64M $NaHCO_3$/1M NaCl solution.

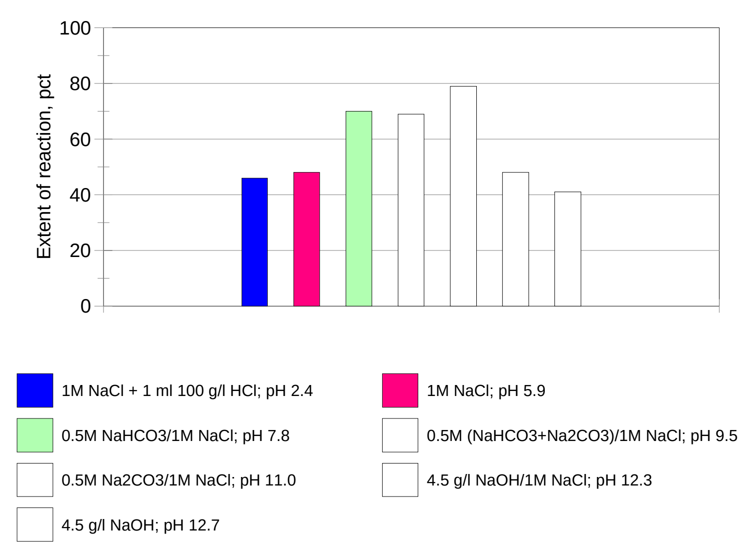

Figure 3. Effect if solution chemistry and pH on extent of reaction. Tests were conducted for 3 hr at 185° C and 115 atm P_{CO2}.

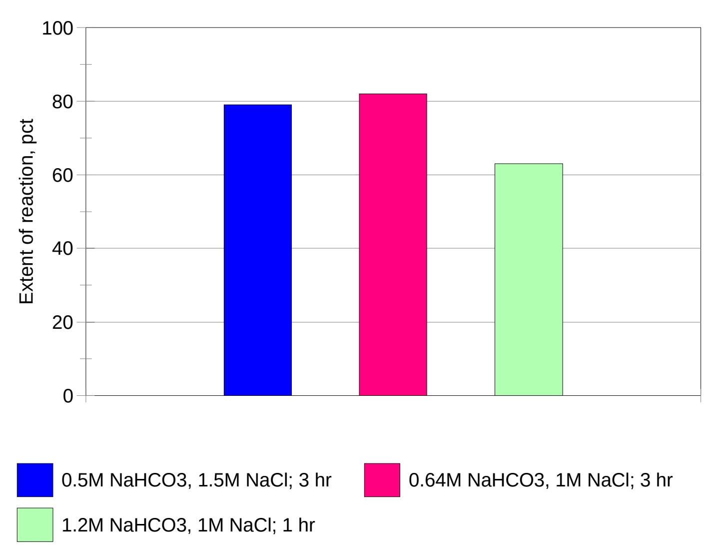

Figure 4. Effect of solution concentration and time on extent of reaction. Tests were conducted at 185° C and 115 atm P_{CO2}.

The $NaHCO_3/NaCl$ solution appears to be very stable in this carbonation environment. Although in-situ pH measurements have not been made under test conditions of high temperature and high pressure, the solutions have nearly constant pre- and post-test pH (~7.8-8.0) and relatively constant CO_2 concentrations (~20 g/L). The following equations represent a possible reaction sequence with the bicarbonate/salt solution chemistry:

$$Mg_2SiO_4 + 2HCO_3^- \rightarrow 2MgCO_3 + SiO_2 + 2OH^- \tag{2}$$

$$OH^- + CO_2 \rightarrow HCO_3^- \tag{3}$$

Bicarbonate anions hydrolyze the magnesium silicate and form the carbonate, free silica (SiO_2), and hydroxyl (OH^-) anions by reaction 2. The OH^- anions react with CO_2 in the solution to reform bicarbonate (reaction 3), thus maintaining relatively constant solution chemistry.

Time, temperature, and pressure

Extent of the carbonation reaction improves with time under similar conditions of temperature and pressure, as would be expected. A goal of this research is to maximize extent of reaction in as short a time as possible, in part by the manipulation of temperature and P_{CO2}.

The carbonation reaction in this system occurs at low pressures and temperatures; the reaction begins during the heating of the autoclave to the operating temperature. Figure 5 shows that more than 20 pct of the silicate may carbonate during heating to 155° C under low P_{CO2}. More than 40 pct extent of reaction was achieved in 3 hr at 155° C and 11 atm P_{CO2}.

Increasing pressure at a given temperature improves the reaction rate. Figure 6 shows that the extent of reaction at 155° C is nearly the same in 30 minutes at 185 atm P_{CO2} as it is in 1 hr at 150 atm. Incremental increases in the extent of reaction at higher pressures may not justify the additional costs that higher pressures imply.

The effect of temperature is more complex in the carbonation

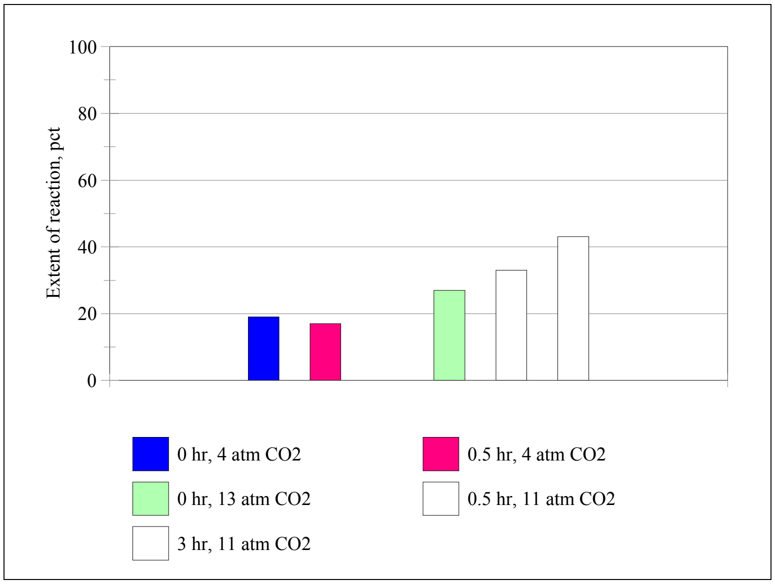

Figure 5. Effect of low pressure CO_2 and time on extent of reaction. Tests were conducted at 155° C in 0.64M $NaHCO_3$/1M NaCl solution.

reaction. Increased temperature improves the kinetics of dissolution of the silicate mineral, but higher temperatures decrease the activity of CO_2 in solution, which inhibits the formation of carbonate minerals. Temperatures between 155° and 185° C provide similar results (figure 7), but at 200° C and above, the detrimental effect of high temperature on carbonation is more noticeable. Increased P_{CO2} does not compensate for the higher temperature (figure 8).

Magnetic separation

Serpentine contains magnetite, a potentially valuable by-product. A single pass through a wet magnetic separator with a permanent magnet produced a magnetic concentrate with a grade of 54 pct total Fe that could conceivably be upgraded to a usable iron ore concentrate for pellet production. The Fe content of the nonmagnetic serpentine was reduced to less than 3 pct. Early results of heat treatments in air and in CO_2 and subsequent carbonation tests suggested that oxidation of the non-silicate iron may inhibit the carbonation reaction. When the magnetite is removed, heat treatment in CO_2 and in air provide similar carbonation results (figure 9). Heat treatment in air would simplify the process and reduce costs.

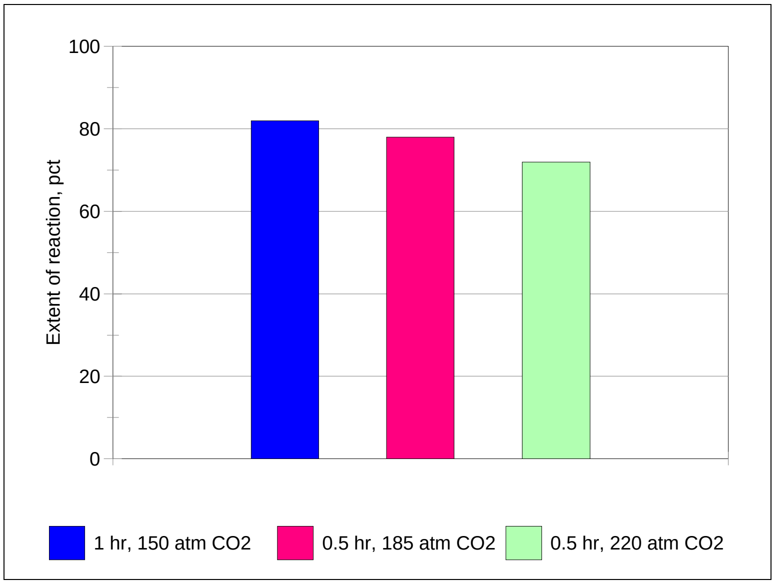

Figure 6. Effect of pressure and time on extent of reaction. Tests were conducted at 155° C in 0.64M $NaHCO_3$/1M NaCl solution.

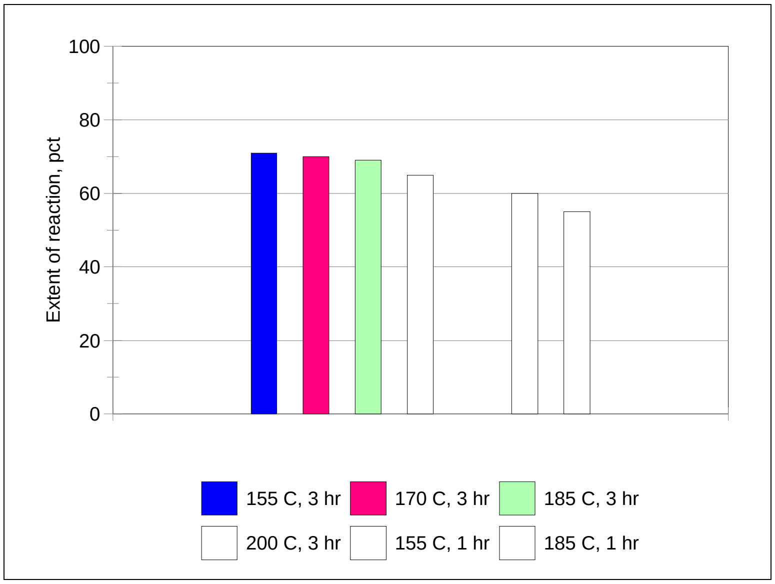

Figure 7. Effect of temperature and time on extent of reaction. Tests represented by the first four bars were conducted in 0.75M $NaHCO_3$/0.5M NaCl solution. Tests represented by the last two bars were conducted in 0.64M $NaHCO_3$/1M NaCl. All tests were conducted at 115 atm P_{CO2}.

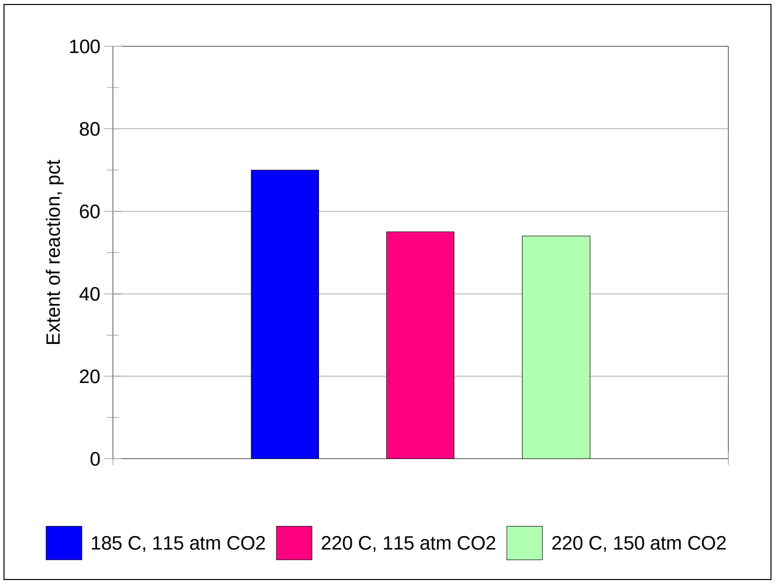

Figure 8. Effect of temperature and pressure on extent of reaction. Tests were conducted for 3 hr in 0.64M $NaHCO_3$/1M NaCl solution.

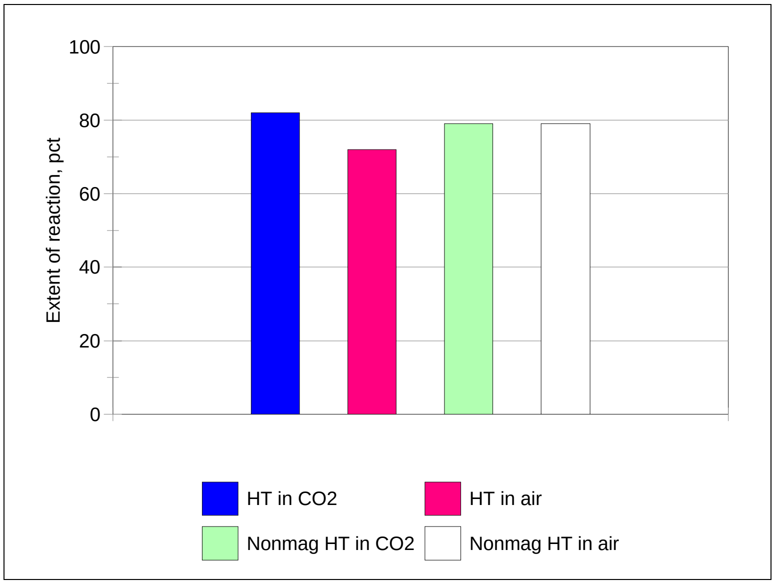

Figure 9. Effect of heat treatment in CO_2 and in air on bulk and nonmagnetic serpentine feed on extent of reaction. Carbonation tests conducted for 1 hr at 155° C and 150 atm P_{CO2}.

The results to date suggest a conceptual flowsheet for a direct-carbonation process as shown in figure 10. Magnesium silicate ore is crushed and ground to size in conventional equipment. Magnetic separation may be incorporated to separate a magnetic iron concentrate. Serpentine (and other hydrated ores) need to be heat treated to remove chemically bound water. The ground and pretreated (if necessary) ore is then slurried with a bicarbonate/salt solution and pumped to an autoclave or pipe reactor, where the slurry is combined with supercritical CO_2 for the carbonation reaction. Solids/liquid separation would be done to separate the magnesium carbonate product and unreacted silicates from the bicarbonate/salt solution. The solution and unreacted CO_2 is recycled with minimal make-up required, and the solids are used for mine reclamation, construction fill, soil amendment, or other possible industrial use.

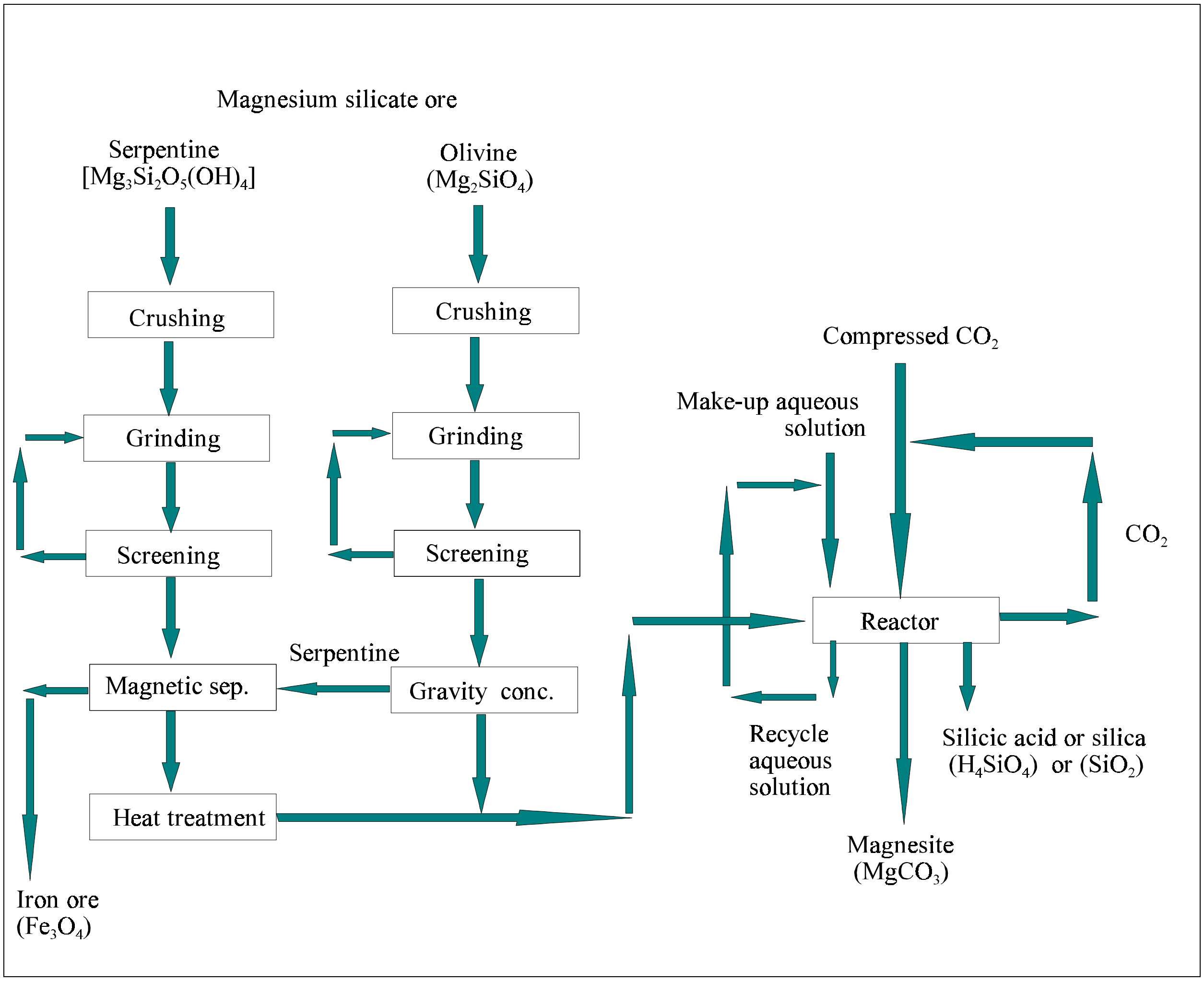

Figure 10. Conceptual process flow diagram for the direct carbonation process.

Summary

The results from studies to date confirm that olivine and serpentine are both amenable to the direct-carbonation process, although serpentine requires heat pretreatment to achieve results comparable to those of olivine. Several sets of test conditions have resulted in conversion of 75 pct or more of the magnesium silicate to magnesium carbonate in 1 hour or less. Combinations of mineral pretreatment with carbonation reaction parameters that provide a high conversion to carbonate in a short time will determine whether the direct-carbonation process is technically and economically feasible.

Investigations of temperature/pressure regimes, modified carbonation solutions, and heat-treatment parameters are in progress to optimize the carbonation reaction. Additional studies are underway to identify chemical pretreatment options that may replace the heat-treatment step for serpentine or otherwise improve the carbonation reaction rate for both olivine and serpentine. Scale-up to a continuous process and engineering and economic studies are planned to determine whether the process is a viable CO_2-sequestration option.

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