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by W.K. O'Connor, D.C. Dahlin, D.N. Nilsen, G.E. Rush , R..P. Walters and P.C. Turner
Albany Research Center
Albany, Oregon

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W.K. O=Connor, D.C. Dahlin, D.N Nilsen,
G.E. Rush, R.P. Walters, and P.C. Turner
Albany Research Center
U.S. Department of Energy
Office of Fossil Energy
1450 Queen Ave SW
Albany, OR 97321

ABSTRACT

Direct mineral carbonation by an ex-situ process in an aqueous system has been investigated over the past two years. The process utilizes a slurry of water mixed with a magnesium silicate mineral, such as olivine [forsterite end member (Mg_2SiO_4)], or serpentine [$Mg_3Si_2O_5(OH)_4$]. This slurry is reacted with sub- or supercritical carbon dioxide (CO_2) to produce magnesite ($MgCO_3$). The CO_2 is dissolved in water to form carbonic acid (H_2CO_3), which dissociates to H^+ and HCO_3^-. The H^+ ion hydrolyzes the mineral, liberating Mg^{2+} cations which react with the bicarbonate to form the solid carbonate. Results of the baseline tests, conducted on ground products of the natural minerals, have demonstrated that the kinetics of the reaction are slow at ambient temperature (22°C) and subcritical CO_2 pressures (below 73 atm). However, at elevated temperature and pressure, coupled with continuous stirring of the slurry and gas dispersion within the water column, significant conversion to the carbonate occurs. Extent of reaction is roughly 90% within 24 hours, at 185°C and partial pressure of CO_2 (P_{CO2}) of 115 atm. Heat pretreatment of the serpentine, coupled with bicarbonate and salt additions to the solution, improve reaction kinetics, resulting in an extent of reaction of roughly 80% within 0.5 hours, at 155°C and P_{CO2} of 185 atm. Subsequent tests are intended to examine various pretreatment options, the carbonation solution characteristics, as well as other mineral groups.

INTRODUCTION

The Albany Research Center (ARC) of the U.S. Dept. of Energy (DOE) has been conducting a series of mineral carbonation tests at its Albany, Oregon facility over the past 2 years as part of a Mineral Carbonation Study Program within the DOE. Other participants in this Program include the Los Alamos National Laboratory (LANL), Arizona State University (ASU), Science Applications International Corporation (SAIC), and the DOE National Energy Technology Laboratory (NETL).

Lackner, et al. (1996, 1997) discussed CO_2 storage as mineral carbonates in prior literature, although these publications describe a process that differs dramatically from the subject process. The direct mineral carbonation process utilizes a slurry of fine particle sized mineral in water, at solids concentrations from 15-30%. Dissolution of the mineral and subsequent carbonation occur in a single unit operation. The theorized reaction equations follow.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (1)$$

$$Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{+2} + H_4SiO_4 \text{ or } SiO_2 + 2H_2O \qquad (2)$$

$$Mg^{+2} + HCO_3^- \rightarrow MgCO_3 + H^+ \qquad (3)$$

The CO_2 is dissolved in water to form carbonic acid (H_2CO_3), which dissociates to H^+ and HCO_3^-(Eq. 1). The H^+ ion hydrolyzes the mineral, liberating Mg^{2+} cations and forming silicic acid or free silica and water (Eq. 2). The free Mg^{2+} cations react with the bicarbonate ions to form the solid carbonate (Eq. 3). An example process flow diagram is shown in Fig. 1. The process has been described in greater detail by O'Connor, et al. (1999, 2000).

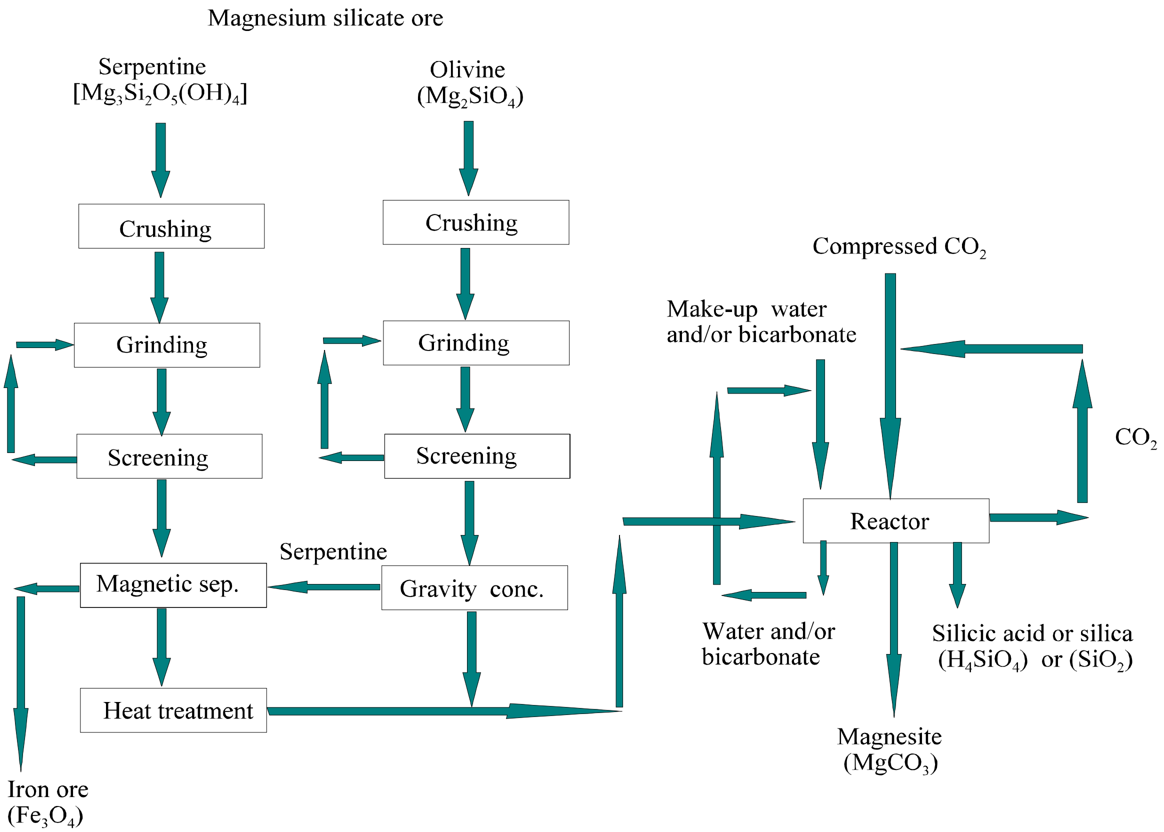

Figure 1: Process flow diagram for the direct carbonation process

The direct mineral carbonation tests have focused thus far on ultramafic minerals as the primary reactants. Geologic studies by Hunter (1941), the IGCP (1977) and Goff (1997) indicate that reserves of these ultramafic minerals are sufficient to provide raw materials for the mineral carbonation of all annual CO_2 emissions for many years. Additional studies conducted at ARC indicate that the mining and milling costs necessary to prepare the minerals for the ex-situ process would be similar to those in the porphyry copper mining industry, at approximately 4-5 U.S. dollars per ton.

FEED MATERIAL ANALYSES

Analyses were acquired for the feed materials used for the direct carbonation tests, with the results reported in table 1. These materials included: naturally occurring olivine (forsterite end member); naturally occurring serpentine; and heat treated serpentine. The product analyses from a magnetic separation step are also included in table 1, along with analyses for the heat treat product from the non-magnetic serpentine fraction.

Table 1: Chemical composition of the feed materials (wt pct)

Oxide	Olivine (forsterite)	Serpentine	Heat treated serpentine	Non-mag serpentine	Magnetic concentrate	HT, non-mag serpentine
Al_2O_3	0.208	0.167	0.268	NA	NA	0.255
CaO	0.070	0.077	0.255	NA	NA	0.152
Cr_2O_3	0.044	NA	0.037	0.058	1.226	NA
FeO	5.966	3.499	3.690	2.367	30.361	2.211
Fe_2O_3	2.558	3.274	4.229	1.501	44.465	1.914
MgO	49.677	40.623	42.175	37.307	10.247	49.677
K_2O	0.007	0.003	0.010	NA	NA	<0.002
SiO_2	41.357	36.155	40.931	37.652	7.509	42.646
Na_2O	0.099	0.010	0.018	NA	NA	<0.002
Volatiles						
C, CO_2	<0.300	0.460	0.250	NA	NA	0.190
C, fixed	0.021	0.020	0.014	NA	NA	0.015
C, total	0.021	0.480	0.264	NA	NA	0.205
H_2O[1]	0.380	0.310	0.48	NA	NA	0.890
H_2O[2]	0.000	13.61	2.676	NA	NA	2.215
Total	100.387	98.208	95.033	78.885	93.808	100.165

[1] Water of dehydration (free moisture).

[2] Chemically-bonded (interstitial) water.

NA: Not analyzed

Magnesium oxide content in the olivine and serpentine were measured at 49.7 weight percent (wt pct) and 40.6 wt pct, respectively. The difference is largely attributable to the high concentration of water (13.6 wt pct) in the serpentine. The serpentine was heat treated to remove the water, resulting in a subsequent increase in magnesium oxide content to 42.2 wt pct. Adding the magnetic separation step prior to heat treatment proved most effective. The magnesium oxide content in the heat treat product from the non-magnetic serpentine fraction, at 49.7 wt pct, duplicated that of the naturally occurring olivine. Emphasis is placed on the magnesium oxide concentration of the feed material, because it is this oxide that reacts with the carbon dioxide to form the carbonate. Thus, feed materials with higher magnesium oxide concentration are preferred. Calculation of the extent of reaction for the direct carbonation tests was based on the concentration of magnesium oxide in the appropriate feed material, and the stoichiometry of the following theoretical equations.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \tag{4}$$

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \tag{5}$$

EXPERIMENTAL RESULTS

Olivine Carbonation

The initial series of olivine carbonation tests included no pretreatment options, other than size reduction to the desired particle size. These tests, exploratory in nature, were intended to produce a baseline set of test parameters for the carbonic acid process, utilizing distilled water as the liquid medium and continuous agitation of the slurry. The addition of gas dispersion in the water column resulted in significant improvement in the extent of reaction, culminating in 91 pct stoichiometric conversion of the silicate to the carbonate in 24 hours, at a temperature of 185˚C and P_{CO2} of 115 atm (Table 2, test SC-25). Formation of the carbonate was confirmed by the identification of magnesite ($MgCO_3$) in the reaction products by X-ray diffraction (XRD) analysis.

Table 2: Test summaries for the direct mineral carbonation tests

Test	Test time, h	T, ˚C	P_{CO2}, atm	Feed material	Particle size, µm	Solution chemistry	Pct stoich. conv.
SC-25	24	185	115	olivine	minus 37	distilled water	91
SC-33	24	185	115	serpentine	minus 37	distilled water	34
SC-34	24	185	115	HT serpentine[1]	minus 37	distilled water	57
SC-39	6	185	115	HT serpentine[2]	minus 37	0.5 M $NaHCO_3$, 1 M NaCl	83
SC-40	6	185	115	olivine	minus 37	0.5 M $NaHCO_3$, 1 M NaCl	84
SC-73	3	185	115	HT serpentine[2]	minus 37	0.5 M $NaHCO_3$, 1 M NaCl	79
SC-83	1	155	150	HT serpentine[2]	minus 37	0.64 M $NaHCO_3$, 1 M NaCl	82
SC-84	0.5	155	185	HT serpentine[2]	minus 37	0.64 M $NaHCO_3$, 1 M NaCl	78
SC-99	1	155	150	HT serpentine[3]	minus 37	0.64 M $NaHCO_3$, 1 M NaCl	79
SC-100	1	155	150	HT serpentine[4]	minus 37	0.64 M $NaHCO_3$, 1 M NaCl	79

[1] Serpentine heat treated in an oxidizing atmosphere.
[2] Serpentine heat treated in a non-oxidizing atmosphere.
[3] Non-magnetic serpentine fraction, heat treated in a non-oxidizing atmosphere.
[4] Non-magnetic serpentine fraction, heat treated in an oxidizing atmosphere.

Particle size was recognized as a major factor determining reaction rate and extent of reaction, because most mineral dissolution reactions are surface controlled. Although coarser sizes can be used effectively, optimal reaction conditions include a particle size of minus 37 microns.

Solution Modification

Modifications to the carbonation solution chemistry were also investigated. This included the use of a bicarbonate/salt mixture, rather than distilled water, which improved the reaction rate dramatically. It is theorized that the bicarbonate ion hydrolyzes the silicate, forming the carbonate, hydroxide (OH^-) ions, and free silica (SiO_2), by the following reaction (Eq. 6).

$$Mg_2SiO_4 + 2HCO_3^- \rightarrow 2MgCO_3 + SiO_2 + 2OH^- \qquad (6)$$

$$OH^- + CO_2 \rightarrow HCO_3^- \qquad (7)$$

The OH^- ion is believed to react immediately with the additional CO_2 being injected into the solution to reform the bicarbonate (Eq. 7), maintaining a relatively constant solution chemistry. This may be described as a buffered solution. The in-situ pH of the solution can not be measured, but pre- and post-test pH measurements remain relatively constant, in the range of 7.7-8.0. This supports the assertion that the solution chemistry remains relatively constant, and verifies that the bicarbonate addition is not consumed in the reaction, but acts as a catalyst.

The salt (NaCl) addition is believed to provide a complexing ion (Cl^-), which combines with Mg^{2+} cations to form several intermediate magnesium chloride compounds. This complexing ion effectively reduces the activity of the Mg^{2+} cation in solution, increasing the solubility of the magnesium silicate mineral.

The use of the sodium bicarbonate and sodium chloride solution, in place of distilled water, resulted in carbonation of naturally occurring olivine to approximately 84% of the stoichiometric maximum in 6 hours, at 185°C and P_{CO2} of 115 atm (Table 2, test SC-40).

Serpentine Pretreatment and Carbonation

During investigations conducted on naturally occurring serpentine, it was demonstrated that heat treating the serpentine, to remove chemically-bonded water and activate the mineral, improved the carbonation results (Table 2, tests SC-33, 34, and 39). Differential thermal and gravimetric analysis, coupled with experimental results from a series of heat treatment and carbonation tests, identified the optimum temperature range for heat treatment to be 600-650°C. The relationship between heat treatment temperature, weight loss from the serpentine, and extent of the carbonation reaction are depicted graphically in Fig. 2.

Weight loss (or water removal) increases significantly above 600°C, with heat treatments conducted below this temperature proving ineffective. Heat treatment temperatures above 650°C can remove up to 1-2 wt pct additional water, but are not considered cost effective. Energy requirements for heat treatment at 600-650°C are estimated at roughly 250 kW•h/ton of serpentine. Steam generation from the heat treatment process represents potential recoverable energy, although current studies are insufficient to determine specific values.

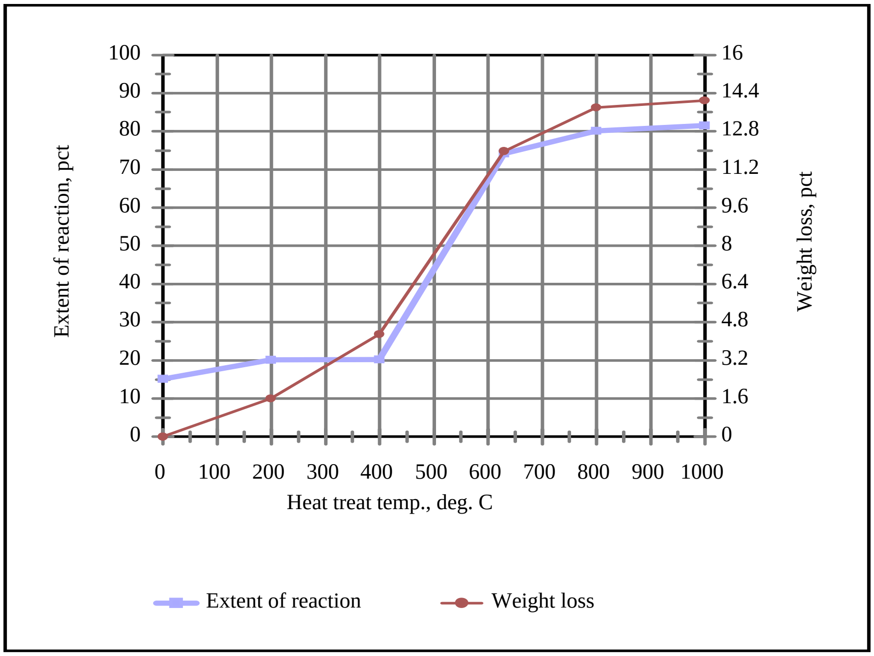

Figure 2: Serpentine weight loss and extent of carbonation versus heat treatment temperature

Magnetic separation was conducted on the serpentine to remove the magnetite (Fe_3O_4) that occurs naturally with the serpentine. This was done for two reasons: 1) the magnetite concentrate represents a marketable product; and 2) heat treatment of the serpentine can be conducted in an oxidizing atmosphere after the magnetite is removed. Oxidation of the magnetite during heat treatment has been shown to inhibit the carbonation reaction. The magnetic separation step proved effective. The concentration of iron oxides in the magnetic concentrate (~74 wt pct total iron oxides) compares favorably with typical iron ore concentrates. Heat treatment tests on the non-magnetic serpentine fraction were conducted under non-oxidizing and oxidizing atmospheres. Results from the subsequent carbonation tests (Table 2, tests SC-99 and 100) demonstrate that the heat treatment atmosphere is no longer critical, once the majority of the magnetite is removed. This simplifies the heat treatment process, and should reduce costs.

The reaction rate for serpentine carbonation has been continuously improved by slight reduction of the reaction temperature, increases in the P_{CO2}, and additional modifications of the solution chemistry (Table 2, tests SC-73, 83, and 84). The optimum reaction conditions identified to date for heat treated serpentine include a sodium bicarbonate and sodium chloride solution chemistry, and reaction temperature of 155˚C at a P_{CO2} of 185 atm. These conditions resulted in serpentine carbonation to approximately 78% of the stoichiometric maximum in 0.5 hours (Table 2, test SC-84). Magnesite was again identified by XRD as the primary phase in the reaction products.

The serpentine feed material is comprised of two minerals in the serpentine group, antigorite and chrysotile, with the antigorite the more abundant of the two. Chrysotile is the asbestos variety of serpentine, and is the primary industrial mineral used for the manufacture of asbestos products. Chrysotile was not identified by XRD in any of the carbonation reaction products from tests using the heat treated serpentine as feed material. This suggests that the favored process utilized for serpentine, heat treatment followed by direct carbonation, destroys the chrysotile, making it an effective method for the remediation of asbestos wastes.

CONCLUSIONS

An aqueous process for the direct carbonation of silicate minerals has been developed as a method for CO_2 storage in solid form. Reaction rates have been improved by utilization of supercritical CO_2, at P_{CO2} of 115-190 atm, temperatures of 155-185˚C, and a solution chemistry including sodium bicarbonate and sodium chloride. Up to 78% stoichiometric conversion of the silicate mineral to the carbonate has been achieved in 30 minutes under these conditions. The carbonation reaction product consists essentially of magnesite (~60 wt pct), free silica (~25 wt pct), and residual silicate (~15 wt pct). Potential uses for the magnesite/silica product include soil amendments, replacing materials such as lime (CaO), limestone ($CaCO_3$), and/or dolomite [$(Ca,Mg)CO_3$]. The hydrophillic nature of the free silica may also improve soil water retention where necessary. A potential by-product from the process is the production of an iron ore concentrate of comparable grade to typical iron ore concentrates. In addition, the results from these studies suggest that the process may be an effective method for the remediation of asbestos wastes, due to the apparent destruction of chrystotile by combined heat treatment and direct carbonation. Future studies are intended to investigate various mineral pretreatment options, alternative reactants, scale-up to a continuous process, and process economics.

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