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CARBON DIOXIDE SEQUESTRATION BY DIRECT AQUEOUS MINERAL CARBONATION

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By

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Carbon Dioxide Sequestration By Direct Aqueous Mineral Carbonation

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ABSTRACT

Carbon dioxide sequestration by an ex-situ, direct aqueous mineral carbonation process has been investigated over the past two years. This process was conceived to minimize the steps in the conversion of gaseous CO_2 to a stable solid. This meant combining two separate reactions, mineral dissolution and carbonate precipitation, into a single unit operation. It was recognized that the conditions favorable for one of these reactions could be detrimental to the other. However, the benefits for a combined aqueous process, in process efficiency and ultimately economics, justified the investigation. The process utilizes a slurry of water, dissolved CO_2, and a magnesium silicate mineral, such as olivine [forsterite end member (Mg_2SiO_4)], or serpentine [$Mg_3Si_2O_5(OH)_4$]. These minerals were selected as the reactants of choice for two reasons: (1) significant abundance in nature; and (2) high molar ratio of the alkaline earth oxides (CaO, MgO) within the minerals. Because it is the alkaline earth oxide that combines with CO_2 to form the solid carbonate, those minerals with the highest ratio of these oxides are most favored. Optimum results have been achieved using heat pretreated serpentine feed material, sodium bicarbonate and sodium chloride additions to the solution, and high partial pressure of CO_2 (P_{CO2}). Specific conditions include: 155°C; P_{CO2}=185 atm; 15% solids. Under these conditions, 78% conversion of the silicate to the carbonate was achieved in 30 minutes. Future studies are intended to investigate various mineral pretreatment options, the carbonation solution characteristics, alternative reactants, scale-up to a continuous process, geochemical modeling, and process economics.

INTRODUCTION

Direct aqueous mineral carbonation has been investigated as part of the CO_2 Mineral Sequestration Working Group within the Department of Energy (DOE). This cooperative research group includes Arizona State University (ASU), the Los Alamos National Laboratory (LANL), the National Energy Technology Laboratory (NETL), Science Applications International Corp. (SAIC), as well as the Albany Research Center (ARC). Lackner, et al. (1996, 1997) discussed CO_2 storage as mineral carbonates, although these publications describe a process that differs dramatically from the direct aqueous process. The direct aqueous 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.

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

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

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

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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). The process has been described in greater detail by Dahlin, et al., (2000), and O'Connor, et al. (2000a, 2000b). A potential process flow diagram is shown in Figure 1.

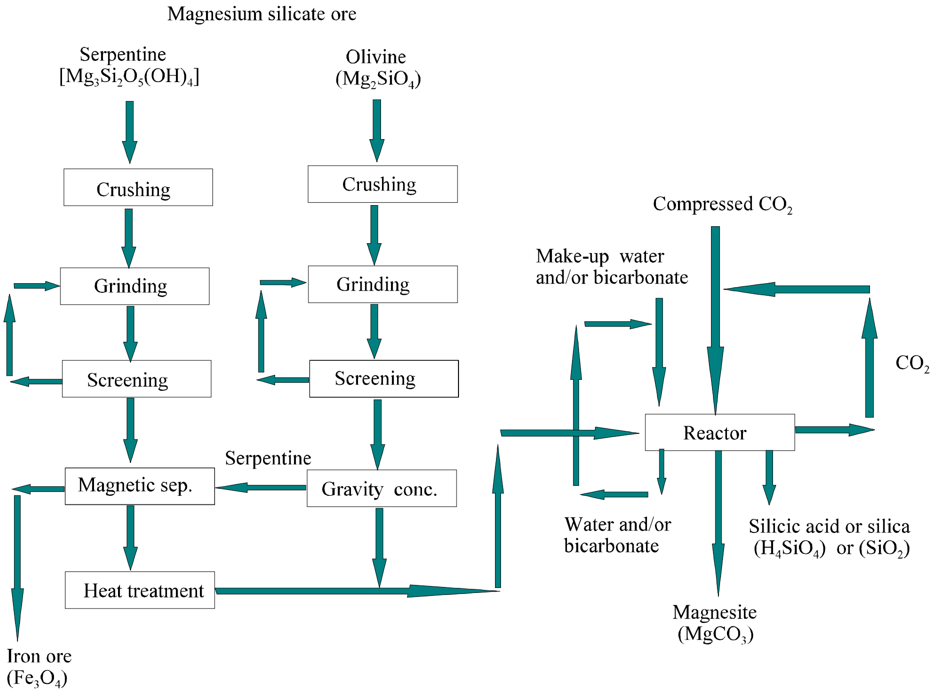

Figure 1.- Flow diagram for the aqueous mineral carbonation process.

Modifications to the carbonation solution chemistry were also investigated. Additions of $NaHCO_3$ and NaCl to the solution improved the reaction rate dramatically. It is theorized that the bicarbonate ion reacts with the silicate, forming the carbonate, hydroxide (OH^-) ions, and free silica (SiO_2), by the following reaction (Eq. 4).

$$Mg_2SiO_4 + 2HCO_3^- \rightarrow 2MgCO_3 + SiO_2 + 2OH^- \qquad (4)$$

$$OH^- + CO_2 \rightarrow HCO_3^- \qquad (5)$$

The OH^- ion may react immediately with the additional CO_2 being injected into the solution to reform the bicarbonate (Eq. 5), 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 development of the aqueous mineral carbonation process has led to effective mineral pretreatment options, improved understanding of the reaction sequence, modification of the solution chemistry, and significant reduction of the reaction time. A broad range of reaction parameters (parametric space) have been investigated, demonstrating that the aqueous mineral carbonation reaction can be achieved at both sub- and supercritical CO_2 partial pressures, in both slightly acidic and buffered solutions. The direct mineral carbonation tests have focused thus far on magnesium silicate minerals as the primary reactants. These magnesium silicate minerals occur in ultramafic sequences around the world, and are by far the most abundant of the high purity alkaline earth silicates. When considering the scale of CO_2 emissions, the only practical approach is to concentrate on feed materials that occur in sufficient quantity to have significant impact the problem. Geologic studies by Hunter (1941), the IGCP (1977) and Goff (1997, 2000) 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. Estimates were made concerning the tonnage of silicate mineral necessary to carbonate 100% of the CO_2 emissions from a single 1 GW coal-fired power plant. Assuming a mean MgO content of the silicate ore of 45 wt pct, 100% ore recovery, and 80% efficiency of the carbonation reaction, a 1 GW coal-fired power plant generating approximately 20 kt/day CO_2 would require over 40 kt/day of ore.

MATERIALS

Several magnesium silicate minerals are suitable for the ex-situ carbonation reaction, including serpentine [$Mg_3Si_2O_5(OH)_4$], enstatite ($MgSiO_3$), and olivine, which actually represents a mineral group encompassing the solid-solution series between magnesium-rich (forsterite, Mg_2SiO_4) and iron-rich (fayalite, Fe_2SiO_4) end members. Each of these minerals occurs in ultramafic complexes, several of which are well documented in North America. 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 (Goff, et al., 1997). 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 Twin Sisters deposit, in the North Cascades of Washington State, includes a currently active olivine mine. Smith (1985) states that this single deposit may contain over 2 billion tons of fresh, unaltered dunite (a rock term defined as a rock comprised of greater than 90% olivine).

Both minerals constitute potential feedstocks for the mineral carbonation process, but a magnesium silicate mineral of high purity, low water content, and high MgO concentration is preferred. Because serpentine is a hydrated mineral and has a lower molar concentration of MgO than olivine, the latter mineral was selected for the initial series of direct carbonation tests. Following these tests, during which basic reaction parameters were established, serpentine was included. Heat pretreatment, necessary to remove the chemically-bonded water from the serpentine, was found to activate the mineral, resulting in a reaction rate exceeding that for olivine. However, the energy demand, estimated at ~200 kW•h/ton, may preclude heat treatment, thus alternative means to activate the serpentine are under investigation. The chemical compositions of the typical olivine and serpentine head samples are included in Table 1.

Magnesium oxide content in the olivine and serpentine head samples were measured at 49.7 weight percent (wt pct) and 40.8 wt pct, respectively. The difference is attributable to the high concentration of chemically-bonded water (13.6 wt pct) in the serpentine. The serpentine was heat treated for 2 hours at 630˚C to remove the water, resulting in a subsequent increase in magnesium oxide content to 45.7 wt pct. 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 feed, and the stoichiometry of the following theoretical equations.

$$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \qquad (6)$$

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad (7)$$

Table 1. Chemical Composition of the Feed and Products (wt pct)

Oxide	Olivine (forsterite)	Serpentine	Heat treated serpentine	SC-25 product	SC-39 product	SC-40 product	SC-84 product	SC-110 product	SC-132 product
Al_2O_3	0.208	0.167	0.270	0.171	0.196	0.132	0.180	0.132	0.139
CaO	0.070	0.077	0.146	0.230	0.356	0.231	0.022	0.231	0.109
Cr_2O_3	0.044	NA	NA	NA	NA	0.247	NA	0.247	0.016
FeO	5.966	3.497	3.394	5.271	0.386	8.576	2.649	8.576	0.591
Fe_2O_3	2.558	3.272	4.544	NA	4.973	<0.010	3.301	<0.010	3.500
MgO	49.677	40.842	45.676	35.507	33.673	36.841	27.672	36.841	38.333
K_2O	0.007	0.003	0.004	NA	0.006	0.005	0.006	0.005	0.010
SiO_2	41.357	36.214	40.500	26.786	28.701	26.357	29.786	26.357	31.716
Na_2O	0.099	0.010	0.010	NA	0.414	0.144	0.492	0.144	0.802
Volatiles									
C, CO_2	<0.300	0.460	0.290	32.300	28.071	29.800	24.700	29.800	20.400
C, fixed	0.021	0.020	0.017	3.691	0.584	0.213	0.014	0.213	<0.010
H_2O^1	0.380	0.310	0.680	NA	0.200	<0.050	0.700	<0.050	1.910
H_2O^2	0.000	13.610	3.203	NA	1.516	0.687	2.886	0.687	4.190
Total	100.387	98.482	98.734	103.956	98.575	100.487	92.407	100.487	101.716

[1] Water of dehydration (free moisture). NA: Not analyzed

[2] Chemically-bonded (interstitial) water.

EXPERIMENTAL PROCEDURES

The initial proof-of-concept tests were conducted in an autoclave with continuous agitation or stirring, while process parameters were monitored and recorded in real time. Liquid CO_2 was added to the vessel prior to heating, at the proper weight to reach the desired pressure at the final operating temperature. The proper weight of CO_2 was calculated in advance using the compressibility factor equation of state. The CO_2 compressibility factor was interpolated from the available literature initially, then modified based on the empirical data. The solubility of CO_2 in water at the desired conditions was also estimated, and included in the final calculation. A detailed description of the procedure is included in previous papers (O'Connor et al., 2000a, 2001).

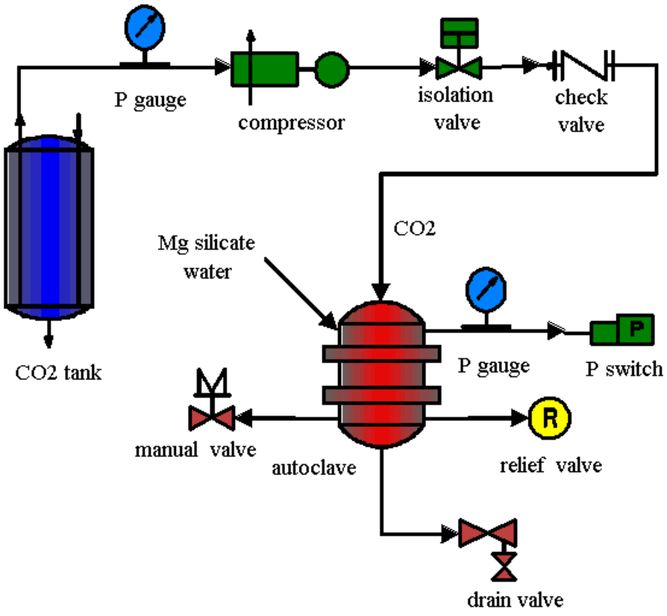

Figure 2.- Schematic of the laboratory apparatus.

Following the initial test series, a new autoclave system (STR) was developed including a CO_2 gas booster pump (compressor) controlled by a pressure switch on the autoclave (Figure 2). The modified test procedure follows.

1. 167 g of mineral reactant and 950 g of distilled water (or bicarbonate/salt solution) poured into the STR;
2. STR sealed, purged with CO_2, stirrer speed 1,000 rpm;
3. STR heated to final operating temperature, stirrer speed increased to 2,000 rpm;
4. CO_2 injected to final operating pressure;
5. additional CO_2 injected as system pressure decreases due to chemical reaction and/or pressure leaks;
6. after specified test time, STR cooled, pressure bled off, slurry removed;
7. slurry filtered, solids dried, weighed, and sampled for analyses, solution sampled for analyses.

All tests conducted in the new system followed this simplified procedure. The inclusion of the gas booster pump permitted operation under relatively constant P_{CO2}, which was not possible in the former system. This minimized the impact of decreasing P_{CO2} on reaction rate and final extent of reaction.

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 direct aqueous mineral carbonation process, and utilized distilled water as the liquid medium and continuous agitation of the slurry. The addition of gas dispersion in the water column, and the ability to operate at constant P_{CO2} (in the new autoclave system), resulted in significant improvement in the extent of reaction. This culminated 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 3).

Table 2. Test Summaries for the Direct Aqueous Mineral Carbonation Tests

Test	Feed material	Particle size, µm	Carbonation conditions			Solution chemistry	Percent stoich. conv.
			Time, hr	T, ˚C	P_{CO2}, atm		
SC-25	olivine	-37	24	185	115	distilled water	91
SC-39	serpentine[1]	-37	6	185	115	0.5 M $NaHCO_3$, 1 M NaCl	83
SC-40	olivine	-37	6	185	115	0.5 M $NaHCO_3$, 1 M NaCl	84
SC-84	serpentine[1]	-37	0.5	155	185	0.64 M $NaHCO_3$, 1 M NaCl	78
SC-110	olivine[2]	-37	1	155	150	0.64 M $NaHCO_3$, 1 M NaCl	52
SC-132	serpentine[1]	-75	1	155	150	0.64 M $NaHCO_3$, 1 M NaCl	58

[1] Heat treated serpentine.

[2] Final stage olivine grind conducted in 1 M NaOH, 1 M NaCl solution.

Modification of the carbonation solution chemistry, to the sodium bicarbonate/sodium chloride solution rather than distilled water, led to a dramatic increase in reaction rate. The bicarbonate solution acts as a

CO_2 carrier, providing abundant bicarbonate ions to react with the Mg^{2+} cations released from the mineral. The bicarbonate concentration remains relatively constant, based on pre- and post-test solution analysis. Apparently, the bicarbonate is continuously regenerated by the injection of CO_2 into the slurry. Reaction time was reduced to 6 hours for test SC-40, with over 80% conversion to the carbonate. The bicarbonate concentration was increased from 0.5 M to 0.64 M, the maximum solubility for $NaHCO_3$ in a 1M NaCl solution at 20˚C. This solubility was selected to simulate the solution concentration most likely to be used in a continuous recycle process. Higher bicarbonate concentrations could be used due to the elevated temperatures used for carbonation. However, these higher concentrations would likely result in solution losses to the solids during solid/liquid separation. Means to reduce reaction times continue to be investigated. The optimum results thus far include a caustic leach added to the final stage grind of the olivine (Table 2, test SC-110). Conversion to the carbonate was ~52% in 1 hour.

Table 3. X-ray Diffraction Analyses for the Feed and Products

Test	Material	Primary	Secondary	Minor	Trace
SC-25	olivine head	forsterite (Mg_2SiO_4)		enstatite	
	carbonation product	magnesite ($MgCO_3$)	forsterite		forsterite, enstatite
SC-39	serpentine head	antigorite [$Mg_3Si_2O_5(OH)_4$]		clinochrysotile [$Mg_3Si_2O_5(OH)_4$]	magnetite (Fe_3O_4) clinochlore ($Mg_5Al_2Si_3O_{14}.4H_2O$)
	heat treat product	forsterite		magnetite antigorite	
	carbonation product	magnesite			magnetite forsterite antigorite
SC-40	olivine head	forsterite		enstatite	
	carbonation product	magnesite		forsterite	enstatite antigorite (?)
SC-84	serpentine head	antigorite		clinochrysotile	magnetite clinochlore
	heat treat product	forsterite		magnetite antigorite	
	carbonation product	magnesite			magnetite forsterite
SC-110	olivine head	forsterite		enstatite	
	carbonation product				
SC-132	serpentine head	antigorite		clinochrysotile	clinochlore
	heat treat product	antigorite	forsterite		clinochlore
	-25 µm product	magnesite		antigorite	forsterite

Primary phase: 40-100% Secondary phase: 20-60% Minor phase: 5-30% Trace phase: 0-10%

Serpentine 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-39, 84 and 132). 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. 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 (Table 3).

ANALYSIS AND DISCUSSION OF RESULTS

Chemical analyses were acquired for the solid products from each of the carbonation tests. A selection of the results are reported in Table 1. The CO_2 concentration in the products, coupled with the identification of magnesite by XRD, provided conclusive evidence that the mineral carbonation process was successful. Samples of the product solids were also prepared for study with the scanning electron microscope (SEM) with wavelength-dispersive X-ray microanalysis (WDX). A brief description of the typical olivine and serpentine reaction products follows.

Olivine Reaction Products

Figure 3 is a backscatter electron (BSE) image of the SC-40 reaction product. The small (<10 µm) rounded particles dispersed throughout the view were identified as magnesite by SEM-WDX. This is indicative of carbonate precipitation, rather than solid-state conversion, as the predominate mechanism for carbonate formation. The composition of the larger grains in the view were of significant interest. A series of SEM-WDX point scans, numbered 1-4 on Figure 3, were collected to determine the C, Fe, Mg, O, and Si concentration in the various particles (Table 4).

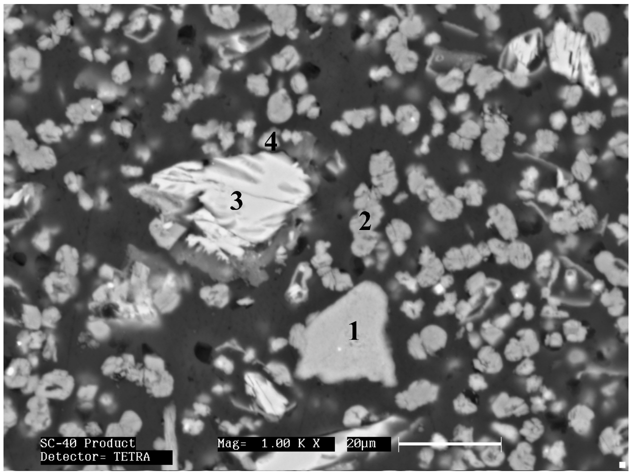

Figure 3. BSE Image of the SC-40 Product.

Table 4. SEM-WDX Microanalyses for SC-40 Product.

Point	Atomic percent					
	C	Fe	Mg	O	Si	Mg/Si
1	3	0.3	20	63	13	3:2
2	26	ND	17	55	1	17:1
3	3	1.3	25	58	12	2.1
4	6	0.3	1	67	26	1:25

ND: Not detected

The analysis for point 1 suggests that this is an altered olivine grain, depleted in Mg, as indicated by the lower Mg/Si ratio, 3:2 compared to that for olivine (forsterite), 2:1. Point 2 provides a typical analysis for the magnesite particles. Silicon content is very low, which suggests that the silica does not agglomerate with or precipitate onto the magnesite particles. The analysis for point 3 indicates that the bright white grain is relatively unaltered olivine, at least at the core. A reaction rim depleted in Mg is obvious at the lower portion of the grain. The grain represented by point 4 is composed primarily of silica, indicative of the separate magnesite and silica particles that make up the fine matrix of the sample. These small (5-10 μm) silica particles may result from attritioning of the coarser, skeletal grains of altered silicate.

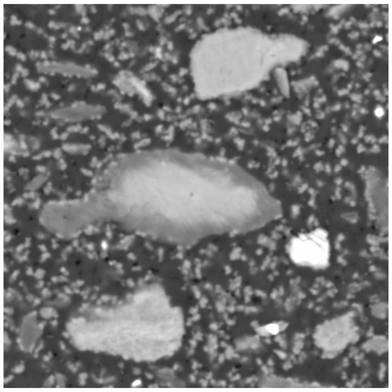
Figure 4a. BSE Image of SC-39 Product (1,000 x).

Serpentine Reaction Products

The character of the magnesite product does not appear to change with increasing extent of reaction. However, alteration of the original silicate mineral is much more pronounced. The reaction products from test SC-39, which achieved 83% stoichiometric conversion of heat pretreated serpentine to carbonate, are depicted in the Figure 4 photo series.

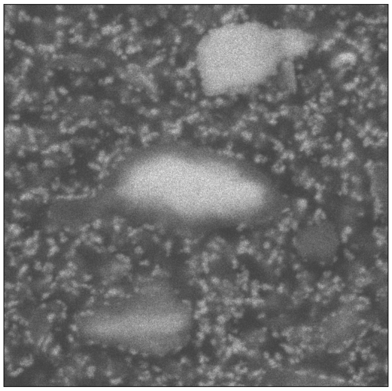
Figure 4b. X-ray map for Mg on SC-39 Product.

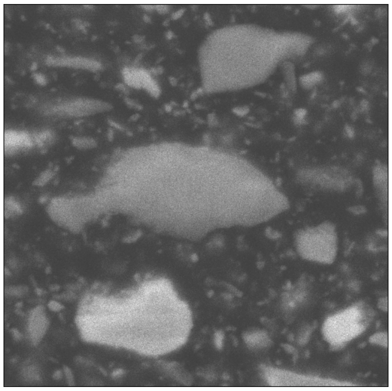
Figure 4c. X-ray map for Si on SC-39 Product.

The large grain in the center of Figure 4a shows a definite alteration rim. The X-ray maps suggest that this alteration rim is depleted in Mg (4b), compared to the core of the grain. The Si concentration appears to be uniform throughout the grain (4c), suggesting that as the Mg^{2+} is removed, the silica is not mobilized, producing a zone enriched in silica. The grain provides strong evidence for a shrinking core model for the reaction.

The large skeletal grain at lower left-center in Figure 4a is composed primarily of silica. SEM-WDX microanalysis conducted on this grain reported a Mg/Si ratio of 3:4. This is half the theoretical Mg/Si ratio of 3:2 for serpentine, and lower than the theoretical ratios for either forsterite or enstatite, This grain could represent the primary fate of the silica, which may form masses of amorphous silica making up the matrix of the highly altered silicate grains. The Si X-ray map (4c) shows that fine particles (<10 μm) composed primarily of silica do occur, but are angular in shape compared to the more rounded magnesite particles. This may be due to attrition of the larger skeletal grains, rather than precipitation from solution. The latter would likely result in the formation of silica gel, which would make filtration difficult. However, filtration rates of the product slurry have exceeded rates that would be expected from a silica gel-bearing slurry, suggesting that the silica is not dissolved.

Reaction Pathway

The characterization study described above provided conclusive evidence for the successful production of magnesium carbonate solids. However, the pathway to this final product was not clear. Several key questions were unanswered, such as: (1) does the conversion of the silicate to carbonate occur in the solid state; (2) what is the primary mechanism for carbonate formation; (3) what intermediate products occur; (4) is the reaction strictly surface controlled, or diffusion limited; (5) is the reaction inhibited by the formation of passive coatings on the particles; and (6) what is the fate of the silica?

Examination of specific test products led to an improved understanding of the reaction pathway, although the results are not yet definitive. The complete study is included in a recent publication by O’Connor, et al (2001). Space is not sufficient to include the entire discussion, but the results are summarized below.

- conversion of the silicate to carbonate does not occur in the solid state, but appears to require mineral dissolution into the aqueous phase
- precipitation is the primary mechanism for carbonate formation
- alteration of the primary magnesium silicate minerals produces silica enriched, magnesium depleted intermediate products
- while the mineral dissolution reaction is likely surface controlled, the formation of silica enriched zones suggests the reaction may be diffusion limited
- formation of silica rims on the reaction surfaces may slow further dissolution
- porous, skeletal grains with extremely high silica content were identified in the reaction products, suggesting that with continued removal of Mg^{2+} cations, the original silicate grains may be converted to masses of amorphous silica

Reaction Kinetics

Three series of carbonation tests were conducted to determine rate curves for the direct mineral carbonation reaction. The time series included tests conducted for 0, 0.5, 1, 3, 6, and 12 hours, on a heat pretreated, nonmagnetic fraction of serpentine, and olivine. Test conditions were kept constant: particle size of 90% minus 75 microns; 155˚C; P_{CO2} =150 atm; stirring speed 1,000 rpm; and 15% solids, in a solution of 0.64 M $NaHCO_3$, 1 M NaCl. A second series was conducted on the olivine at 2,000 rpm, with all other parameters held constant, to examine the effect of agitation on reaction kinetics. The series are included in Figure 5.

The much higher reactivity of the heat pretreated serpentine is apparent from the curves. The “zero” hour tests were conducted to determine the extent of reaction that occurs while heating the system to operating temperature. After purging the vessel, a residual P_{CO2} of ~10 atm remains. This, along with the bicarbonate solution, provide sufficient reactant to carbonate a significant portion (~31%) of the heat pretreated serpentine before reaching final conditions. This is not the case for the olivine, however. No reaction was apparent after 1 hour on the olivine, at a stirring speed of 1,000 rpm. This can be overcome to some extent by increasing the stiring speed to 2,000 rpm. The greater degree of agitation may help to produce more reactive fines. However, with time, the higher stirring speed appears to have little effect on reaction rate. It is obvious from Figure 5 that either some pretreatment of the olivine, or a more aggressive leach solution, is necessary to shift its rate curve to the left.

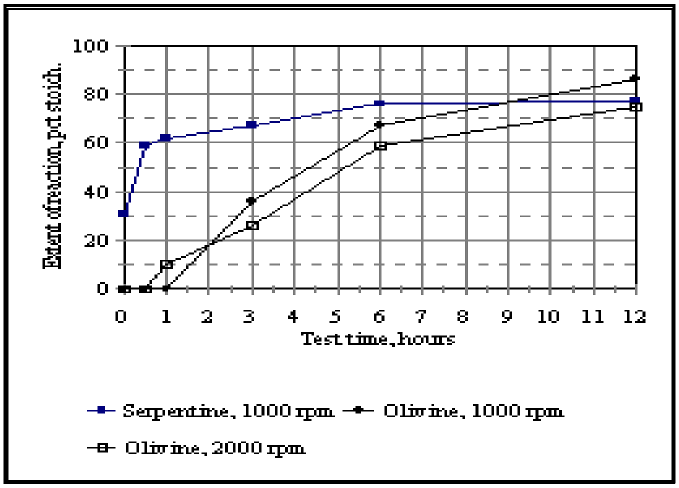

Figure 5.- Reaction rate curves for the mineral carbonation process.

Serpentine Reactivity

Variations in the Loss on Ignition (LOI) for the serpentine heat treatment products appear to play the predominate role in determining the extent of carbonation, when all other parameters are held constant (Figure 6). Significant variations in LOI for the various heat treatment products, from ~3 to ~6 wt pct, were identified as the primary reason for the reduced extent of carbonation. These irregularities in LOI occurred even though all heat treatment tests were conducted at “identical” conditions. At the bench-scale, minor variations in operating conditions from heat to heat are unavoidable, and they appear to be significant enough to effect the final LOI. Because the serpentine head material contains ~13.5 wt pct chemically bonded water, every 1% LOI in the heat treatment product represents about 7% of mineral that is still hydrated. These studies strongly indicate that the serpentine containing chemically-bonded water will not carbonate, at least not at the more rapid rate. Thus, every 1% LOI in the heat treatment product (carbonation feed) reduces the effective carbonation potential by about 7%. The relationship between the residual LOI and extent of carbonation appears to be linear, so it may be possible to compare all prior and subsequent tests at a normalized LOI, perhaps 3.5 wt pct. This would eliminate the apparent variations in extent of reaction due to imperfections in heat treatment.

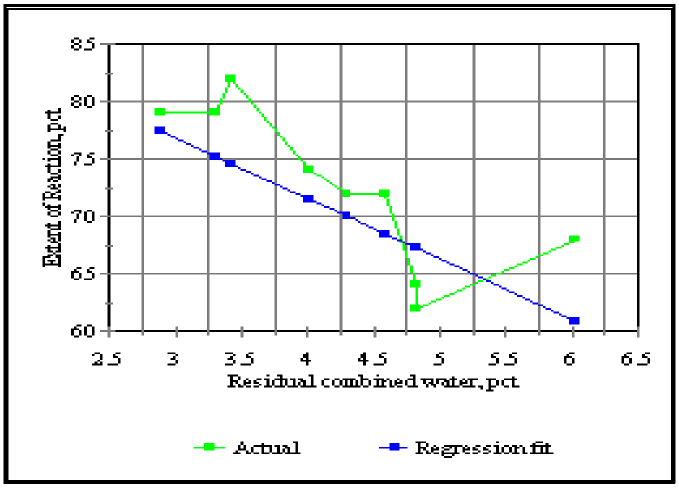

Figure 6.- Relationship between residual LOI and extent of carbonation.

Reaction Surface

Surface area measurements using the BET gas absorption method were conducted on the three primary mineral reactants, antigorite serpentine, lizardite serpentine, and olivine. Determination of the mineral surface area permits normalization of the mineral reaction rates. Specific surface area measurements for the various materials, and reaction rates, in $g/m^2/h$, are included in Table 5.

Table 5.- BET surface area measurements for the various mineral reactants.

Material	Specific Surface Area, m^2/g		Total[1] SA, m^2	Mg[2] mass, g	Mg[3] conv., g	Conv. rate, $g/m^2/h$
	Head	HT product				
Antigorite serpentine, -37 micron	6.0	19.1	3190	45	37	0.012
Antigorite serpentine, -75 micron	6.1	18.9	3156	45	33	0.010
Lizardite serpentine, -37 micron	8.3	11.2	1870	38	17	0.009
Olivine, -37 micron	2.1		351	50	7	0.019

[1] Total surface area for tests using 167 g of mineral reactant.

[2] Mass concentration of Mg in carbonation feed.

[3] Mass of Mg converted to the carbonate (best results for 1 hour carbonation tests).

The heat treat (HT) product comprised the feed material for the serpentine carbonation tests, while the olivine head comprised the feed material for the olivine carbonation tests. Conversion rates, in grams of Mg converted to the carbonate per m^2 per hour, were calculated for the most successful carbonation tests, 1 hour in duration, on each feed material. The normalized reaction rates show that the olivine has the highest relative rate of reaction, which appears to contradict the rate curves from figure 5. Actually, the normalized reaction rates merely confirm the significant impact surface area has on the mineral dissolution rates. As shown by XRD, heat treatment of the serpentines produces forsterite (olivine), but this "synthetic" olivine has much greater surface area than the natural olivine. Removal of the chemically-bonded water from the serpentine appears to produce a highly porous product, which greatly increases its effective surface area, and consequently, its reactivity. Olivine pretreatment studies may not be able to increase the porosity of the natural occurring mineral, but may include chemical attack along grain boundaries, or destabilization of the structure by ultrasonic or microwave treatment, which may increase the surface exposed to attack by the carbonation solution.

Product Size and Phase Distribution

Particle size distribution for the feed and products from test SC-132 are included in Figure 7. Some size reduction as a result of the carbonation test is apparent. The distribution curve for CO_2 is also included in Figure 7. Over 99% of the CO_2 reported to the minus 500 mesh (25 micron) product, which supports the conclusion made previously that the magnesite product is confined to the fine fractions. Magnesite was only identified in the minus 25 micron fraction by XRD.

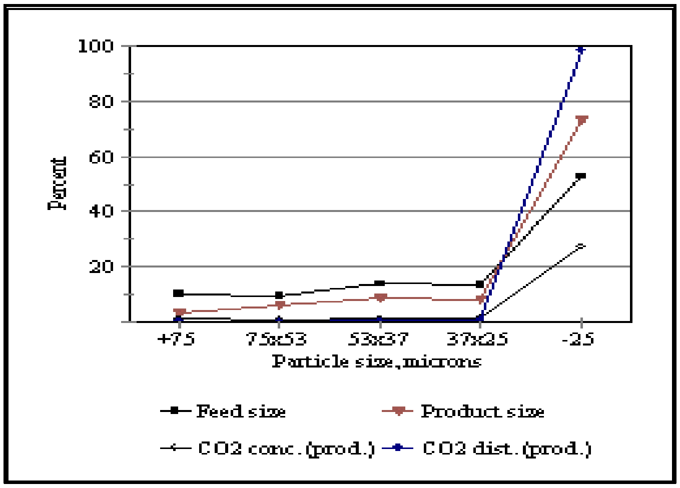

Figure 7.- Particles size and CO_2 distributions.

Using the concentrations for CO_2, Mg, and Si for each of the size fractions, the relative percentages of Mg and Si occurring as specific phases was calculated (Figure 8). To perform the calculations, several assumptions were necessary: (1) all CO_2 was assumed to be present as $MgCO_3$; (2) residual silicate was assumed to be present as serpentine, with a Mg/Si ratio of 3:2; and (3) excess Si was assumed to be present as free silica. The results are very informative. Virtually all of the Mg in the plus 25 micron size fractions is present as the silicate mineral, while the Mg phase changes abruptly to the carbonate in the minus 25 micron fraction. This suggests that classification of the product solids by hydrocyclone could effectively separate the unreacted silicate from the magnesite product, providing an effective means to recycle the silicate mineral through the process.

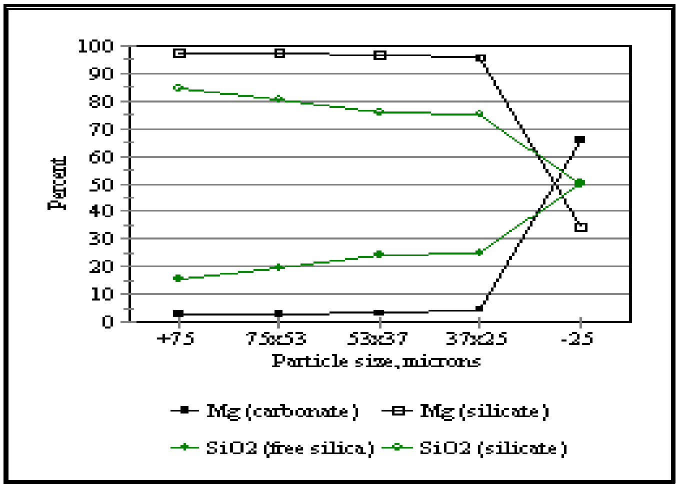

Figure 8.- Percentage of Mg and Si as specific phases.

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 115-185 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. The basic understanding of the mineral dissolution and carbonate precipitation reaction paths has been improved, although this remains a major area of continued study. Several key conclusions to date include:

- conversion of the silicate to the carbonate requires mineral dissolution into the aqueous phase
- precipitation is the primary mechanism for carbonate formation
- the mineral dissolution reaction is likely surface controlled
- formation of silica enriched, magnesium depleted zones suggests the reaction may be diffusion limited
- removal of chemically-bonded water from serpentine is necessary to achieve carbonation at high efficiencies and rapid rates
- pretreatment of olivine to increase the reactive surface should improve reaction kinetics
- the product solids can be classified by hydrocyclone, making recycle of the unrreacted silicate possible

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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