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# RESEARCH STATUS ON THE SEQUESTRATION OF CARBON DIOXIDE BY DIRECT AQUEOUS MINERAL CARBONATION

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by W.K. O'Connor, D.C. Dahlin, D.N. Nilsen, S.J. Gerdemann, G.E. Rush, R.P. Walters, and  
P.C. Turner

Albany Research Center  
Albany, Oregon



# **Research Status on the Sequestration of Carbon Dioxide by Direct Aqueous Mineral Carbonation**

**W.K. O'Connor<sup>1</sup>, D.C. Dahlin, D.N Nilsen,  
S.J. Gerdemann, G.E. Rush, R.P. Walters, and P.C. Turner**

Albany Research Center  
Office of Fossil Energy, USDOE  
1450 Queen Ave SW, Albany, OR 97321

<sup>1</sup>[oconnor@alrc.doe.gov](mailto:woconnor@alrc.doe.gov)

## **Abstract**

Direct aqueous mineral carbonation has been investigated as a process to convert gaseous CO<sub>2</sub> into a geologically stable, solid final form. The process utilizes a solution of distilled water, or sodium bicarbonate (NaHCO<sub>3</sub>), sodium chloride (NaCl), and water, mixed with a mineral reactant, such as olivine (Mg<sub>2</sub>SiO<sub>4</sub>) or serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]. Carbon dioxide is dissolved into this slurry, by diffusion through the surface and gas dispersion within the aqueous phase. The process includes dissolution of the mineral and precipitation of magnesium carbonate (MgCO<sub>3</sub>) in a single unit operation. Mineral reactivity has been increased by pretreatment of the minerals. Thermal activation of serpentine can be achieved by heat pretreatment at 630°C. Carbonation of the thermally activated serpentine, using the bicarbonate-bearing solution, at T=155°C, P<sub>CO2</sub>=185 atm, and 15% solids, achieved 78% stoichiometric conversion of the silicate to the carbonate in 30 minutes. Recent studies have investigated mechanical activation as an alternative to thermal treatment. The addition of a high intensity attrition grinding step to the size reduction circuit successfully activated both serpentine and olivine. Over 80% stoichiometric conversion of the mechanically activated olivine was achieved in 60 minutes, using the bicarbonate solution at T=185°C, P<sub>CO2</sub>=150 atm, and 15% solids. Significant carbonation of the mechanically activated minerals, at up to 66% stoichiometric conversion, has also been achieved at ambient temperature (25°C) and P<sub>CO2</sub> ≈ 10 atm.

## **Introduction**

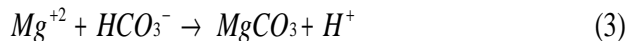
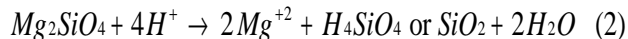
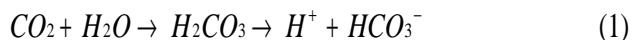
Carbon dioxide gas generated by the combustion of fossil fuels is considered one of the most significant of the greenhouse gases, with CO<sub>2</sub> emissions from fossil fuels alone estimated at 6 GtC/year (Freund and Ormerod, 1997). Means to reduce the CO<sub>2</sub> emissions from the energy and/or process industries has become increasingly emphasized as a primary environmental concern. This can be achieved by efficiency improvements in fossil-fuel-fired power plants, use of alternative energy technologies, sequestration of CO<sub>2</sub>, or some combination of these methods. Due to the availability of fossil fuel resources, it is anticipated that they will continue to play a significant role in the world's energy economy well into the next century. Thus, emphasis must be placed on improving the combustion efficiency of the fossil-fuel-fired power plant, as well as on methods to sequester the CO<sub>2</sub> emitted from these plants.

Sequestration can take many forms, including: 1) forestation, where CO<sub>2</sub> is removed from the

atmosphere by biological activity; 2) aquifer storage, in which the CO<sub>2</sub> is injected into terrestrial aquifers where it is trapped hydrodynamically; 3) deep sea storage, where the CO<sub>2</sub> is injected into the ocean at approximately 3,000 meter depths, where it is believed to remain stable; and 4) mineral carbonation, in which the CO<sub>2</sub> is reacted with minerals to form solid carbonates. In this final form of sequestration the mineral carbonates are stable over geologic time periods (millions of years), rather than the hundreds to thousands of years of storage life expected for the first three forms of sequestration.

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<sub>2</sub> storage as mineral carbonates, 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.



The CO<sub>2</sub> is dissolved in water to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which dissociates to H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> (Eq. 1). The H<sup>+</sup> ion hydrolyzes the mineral, liberating Mg<sup>2+</sup> cations and forming silicic acid or free silica and water (Eq. 2). The free Mg<sup>2+</sup> cations react with the bicarbonate ions to form the solid carbonate (Eq. 3). A potential process flow diagram is shown in Figure 1. The process has been described in greater detail by Dahlin, et al., 2000.

Modifications to the carbonation solution chemistry were also investigated. Additions of NaHCO<sub>3</sub> and NaCl to the solution improved the reaction rate dramatically, producing a buffered solution. Although the in-situ pH of the solution has not been measured, pre- and post-test pH measurements remain relatively constant, in the range of 7.7-8.0. This suggests that the bicarbonate concentration remains relatively constant, perhaps being regenerated by CO<sub>2</sub> injection. A theorized reaction sequence for the modified solution follows (Eq. 4-5).



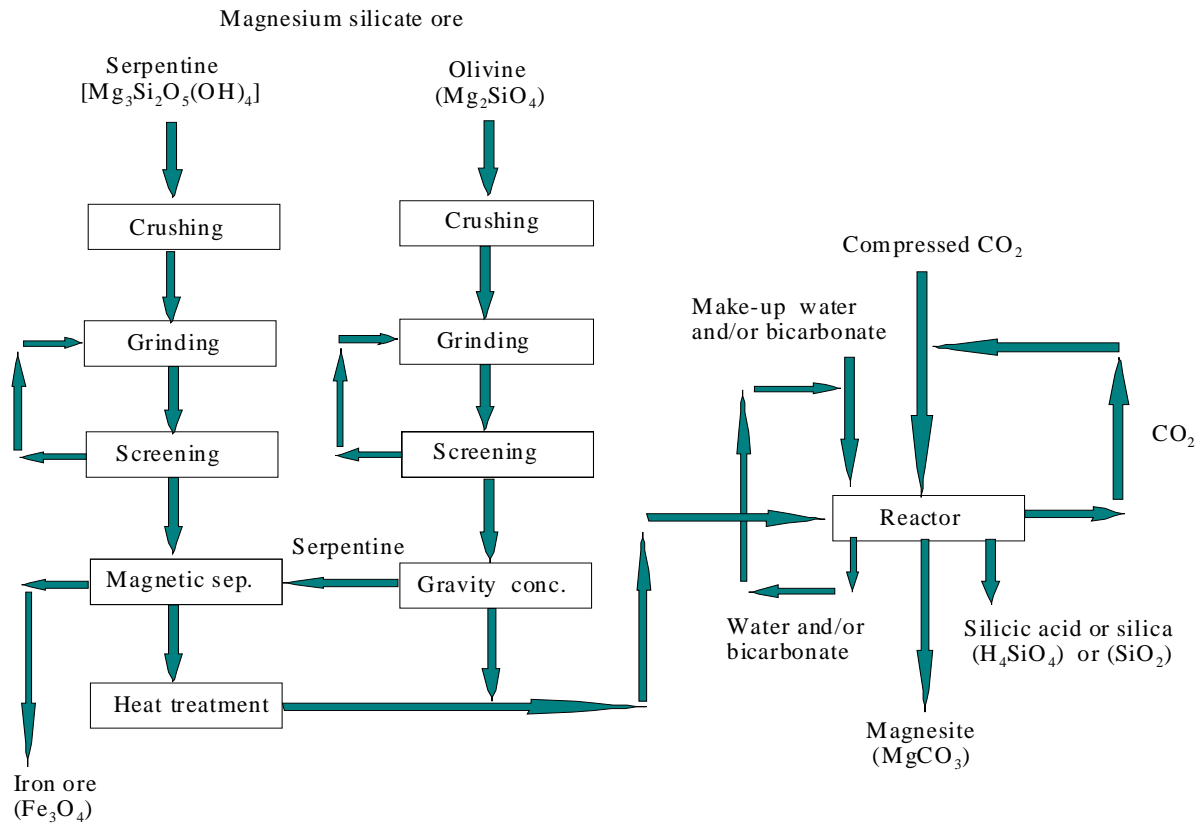


Figure 1.- Potential process flow diagram.

## Materials

The direct mineral carbonation tests have focused thus far on ultramafic minerals, primarily magnesium silicates, as the primary reactants. Several magnesium silicate minerals are suitable for the process, including serpentine [ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ], enstatite ( $\text{MgSiO}_3$ ), and olivine, which actually represents a mineral group encompassing the solid-solution series between magnesium-rich (forsterite,  $\text{Mg}_2\text{SiO}_4$ ) and iron-rich (fayalite,  $\text{Fe}_2\text{SiO}_4$ ) end members. 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  $\text{CO}_2$  emissions for many years. Mining and milling cost studies conducted at ARC indicate that these costs 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  $\text{CO}_2$  emissions from a single 1 GW coal-fired power plant. Assuming a mean  $\text{MgO}$  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  $\text{CO}_2$  would require over 40 kt/day of ore.

The chemical compositions of the typical olivine and serpentine head samples, and a selection of

pretreatment and carbonation products, are included in Table 1. Magnesium oxide concentration in the olivine and serpentine head samples were measured at 49.7 and 40.8 wt pct, respectively. The difference is attributable to the chemically-bonded water (13.6 wt pct) in the serpentine. Feed materials with higher magnesium oxide concentration are preferred because it is this oxide that reacts with the CO<sub>2</sub> to form the carbonate. Calculation of the extent of reaction for the carbonation tests was based on the molar concentration of magnesium oxide in the feed, and the stoichiometry of the following theoretical equations.

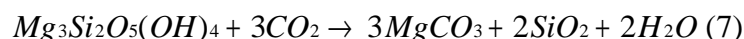
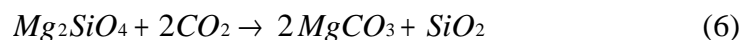


Table 1.-Chemical composition of the typical feed and selected products (wt pct).

Oxide	Olivine (forsterite)	Attritted olivine	Serpentine	Heat treated serpentine	Attritted serpentine	Carbonation products			
						SC-39	SC-40	SC-251	SC-257
Al <sub>2</sub> O <sub>3</sub>	0.208	0.208	0.167	0.270	0.146	0.196	0.132	0.176	0.142
CaO	0.070	0.197	0.077	0.146	0.075	0.356	0.231	0.101	0.135
Cr <sub>2</sub> O <sub>3</sub>	0.044	0.025			0.164		0.247	0.110	0.191
FeO	5.970	8.280	3.500	3.390	2.210	0.386	8.580	1.110	3.840
Fe <sub>2</sub> O <sub>3</sub>	2.560	0.329	3.270	4.540	2.780	4.970	<0.010	2.360	1.840
MgO	49.700	46.800	40.800	45.700	38.700	33.700	36.800	27.300	32.000
K <sub>2</sub> O	0.007	0.003	0.003	0.004	0.037	0.006	0.005	0.002	0.006
SiO <sub>2</sub>	41.400	39.900	36.200	40.500	36.900	28.700	26.400	25.900	27.900
Na <sub>2</sub> O	0.099	0.246	0.010	0.010	0.008	0.414	0.144	0.527	0.019
Volatiles									
C, CO <sub>2</sub>	<0.300	0.320	0.460	0.290	1.290	28.100	29.800	19.400	27.800
C, fixed	0.021	0.085	0.020	0.017	0.054	0.584	0.213	0.260	0.279
H <sub>2</sub> O <sup>1</sup>	0.380	0.330	0.310	0.680	1.050	0.200	<0.050	4.970	0.580
H <sub>2</sub> O <sup>2</sup>	0.000	1.660	13.600	3.200	12.900	1.520	0.687	19.500	1.840
Total	100.400	98.400	98.400	98.700	96.300	99.100	103.200	101.700	96.600

<sup>1</sup> Water of dehydration, measured as the weight loss after 1 hour at 105°C, in air.

<sup>2</sup> Chemically-bonded water, measured as the weight loss after 1 hour at 1,000°C, in argon, less other volatiles.

Both olivine and serpentine constitute potential feedstocks for the mineral carbonation process, although separate, mineral-specific process paths are necessary for successful carbonation. Heat pretreatment, which removes the chemically-bonded water from the serpentine, was found to activate the mineral. However, the energy demand is excessive, estimated at ~200-250 kW•h/ton. Olivine requires no heat pretreatment, but has exhibited a 1-3 hour incubation period before significant carbonation occurs. Thus, means to activate the minerals have been under continued investigation. Chemical pretreatment has not been effective to date, but the addition of an attrition grinding step to the grinding circuit has successfully activated both serpentine and olivine. Attrition grinding is also energy intensive, and may not be scaleable to the process demands. Still, the initial mechanical activation results encourage further study.

## Experimental Method

The initial proof-of-concept mineral carbonation tests were conducted in an autoclave with continuous agitation or stirring, while process parameters were monitored and recorded in real time. Liquid  $\text{CO}_2$  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  $\text{CO}_2$  was calculated in advance using the compressibility factor equation of state. The  $\text{CO}_2$  compressibility factor was interpolated from the available literature initially, then modified based on the empirical data. The solubility of  $\text{CO}_2$  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).

Following the initial test series, a new autoclave system (STR) was developed including a  $\text{CO}_2$  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 premixed bicarbonate/salt solution) poured into the STR;
2. STR sealed, purged with  $\text{CO}_2$ , stirrer speed set at 1,000-2,000 rpm;
3. STR heated to final operating temperature;
4.  $\text{CO}_2$  injected to final operating pressure;
5. Additional  $\text{CO}_2$  injected as system pressure decreases due to reaction and/or pressure leaks;
6. After specified test time, STR cooled, pressure bled off, slurry removed;
7. Slurry filtered, solids dried, weighed, solids and solution sampled for analyses.

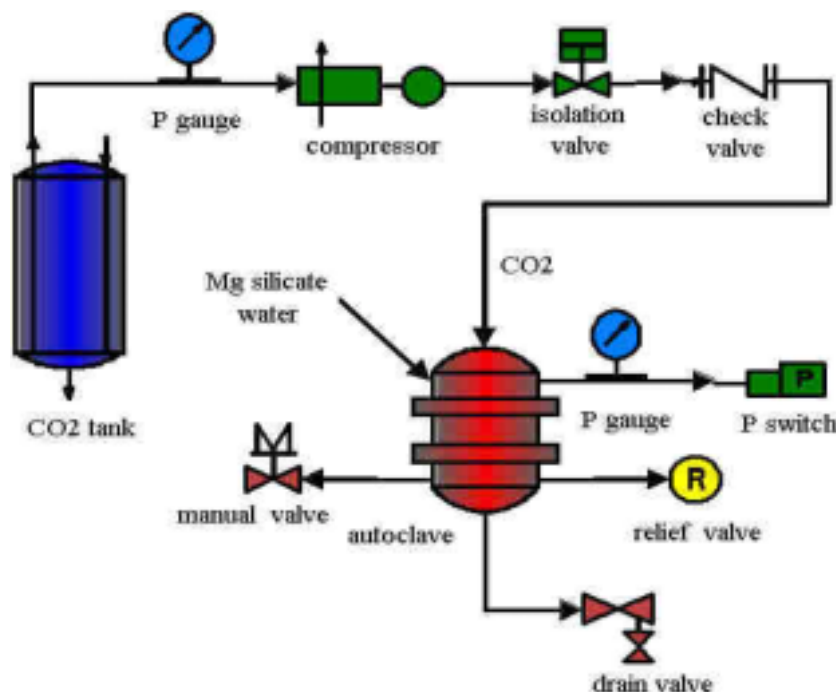


Figure 2.- Reactor schematic.

All tests conducted in the new system at elevated temperature and pressure followed this simplified procedure. The inclusion of the gas booster pump permitted operation under relatively constant  $P_{\text{CO}_2}$ , which minimized the impact of decreasing  $P_{\text{CO}_2}$  on reaction rate and final extent of reaction. Tests conducted at ambient temperature and reduced pressure followed these same procedures, omitting step 3.

## Results and Discussion

### *Summary of Prior Research*

A selection of mineral carbonation tests results reported previously is included in Table 2. Initially, preparation of the mineral reactants consisted of size reduction only, and distilled water was used as the aqueous medium. However, due to the extended reaction times necessary to achieve significant conversion (Table 2, SC-25 and 32), pretreatment methods were investigated to activate the minerals. In parallel to the pretreatment studies, modifications to the carbonation solution were also investigated, finally settling on a buffered solution containing various concentrations of  $\text{NaHCO}_3$  and  $\text{NaCl}$ . Reaction times were reduced to 6 hours using this modified solution and a heat pretreatment step for serpentine but no further pretreatment of olivine (Table 2, SC-39 and 40). Reaction times for heat pretreated serpentine were reduced further by optimizing the reaction temperature and increasing  $P_{\text{CO}_2}$  (Table 2, SC-84). However, chemical pretreatment of olivine met with more limited success (Table 2, SC-113).

Table 2.- Summaries for the aqueous mineral carbonation tests.

Test	Feed material	Particle size, $\mu\text{m}$	Carbonation conditions			Carbonation solution	Percent stoich. conv.
			Time, hr	T, $^{\circ}\text{C}$	$P_{\text{CO}_2}$ , atm		
SC-25	olivine	-37	24	185	115	Distilled water	91
SC-32	serpentine	-37	24	185	115	Distilled water	34
SC-39	serpentine <sup>1</sup>	-37	6	185	115	0.5 M $\text{NaHCO}_3$ , 1 M $\text{NaCl}$	83
SC-40	olivine	-37	6	185	115	0.5 M $\text{NaHCO}_3$ , 1 M $\text{NaCl}$	84
SC-84	serpentine <sup>1</sup>	-37	0.5	155	185	0.64 M $\text{NaHCO}_3$ , 1 M $\text{NaCl}$	78
SC-113	olivine <sup>2</sup>	-37	1	155	150	0.64 M $\text{NaHCO}_3$ , 1 M $\text{NaCl}$	38

<sup>1</sup> Heat pretreated serpentine (1 hour at  $630^{\circ}\text{C}$ , in argon).

<sup>2</sup> Final stage olivine grind conducted in 1 M  $\text{NaOH}$ , 1 M  $\text{NaCl}$  solution.

Thermal treatment of serpentine was discussed in detail in a previous publication (O'Connor et al, 2000a). Thermal analysis of the serpentines, coupled with empirical data compiled from a series of time and temperature tests, identified the optimal heat treatment conditions, namely,  $630^{\circ}\text{C}$  for 1 hour duration, in air. Magnetic separation prior to heat treatment filled a dual role, producing a potentially marketable iron ore by-product, while removal of the magnetite limited oxidation of the serpentine during heat treatment. Excessive oxidation of the iron was shown to inhibit carbonation, but the magnetic separation step permitted all subsequent heat treatments to be conducted in an oxidizing atmosphere. Unfortunately, the heat pretreatment step carries a heavy energy penalty, estimated at 200-250  $\text{kW}\cdot\text{h}/\text{ton}$ .

Olivine pretreatment studies included the combination of chemical pretreatment with size reduction. Final stage wet grinding in a caustic solution (1 M  $\text{NaOH}$ , 1 M  $\text{NaCl}$ ) proved most effective, although even the best results were insufficient (Table 2, SC-113). Ultrasonic pretreatment also failed to activate the mineral. Because thermal pretreatment appeared too energy-intensive, and chemical pretreatment ineffective, subsequent studies were focussed on mechanical means to improve the mineral reactivity.

### *Mechanical Activation of Serpentine and Olivine*

The investigation of the mineral carbonation process has progressed from both technical and economical perspectives. Technical viability is of little use without the potential for practical application, the latter being driven almost exclusively by economics. With this in mind, and considering the potential scale of operations, size reduction of the mineral reactants plays a pivotal role in the feasibility of the overall process, thus size reduction to the maximum size possible is preferred. For this reason, the size reduction conducted for the initial carbonation test series, to minus 37 microns (400 mesh), was considered excessive by some reviewers. Subsequently, the mineral reactant particle size was increased to minus 75 microns (200 mesh), and efforts were made to improve the mineral reactivity without further mechanical size reduction.

As summarized in the previous section, non-mechanical activation of the mineral reactants has proved ineffective, either by technical and/or economic considerations. However, thermal activation of serpentine was technically effective, and efforts to better understand the thermally-activated material were initiated. Alternatives to thermal treatment were eventually limited to mechanical processing, which has recently become the focus of the pretreatment studies.

The enhancement of serpentine solubility by mechanical treatment has been discussed previously by Zhang, et. al, (1996). Dry grinding imparted a structural change, from a crystalline state to an amorphous one, with enhancement of the extraction of both magnesium and silicon from the mechanically activated serpentine by acid solutions. Although the aqueous mineral carbonation process currently utilizes buffered, slightly alkaline, rather than acidic solutions, the potential for mechanical activation of the magnesium silicate minerals was still applicable.

Mechanical activation may be possible by extended grinding times in conventional conical ball mills, or may require more intensive processes, such as attrition grinding, fluid energy milling, or jet pulverization. ARC was equipped with a rotating disc attrition machine, which was used for the initial proof-of-concept studies. Head samples of the minus 75 micron serpentine and olivine were attrition ground for 24 hours to evaluate the impact of high intensity grinding on the mineral reactivity. Chemical compositions of the attrition products were included in Table 1.

### *Serpentine Activation*

The impact of attrition grinding on the mineral reactivity was dramatic, with a summary of the mineral carbonation test results included in Table 3. Figure 3 includes carbonation time series (0.25, 0.5, 1, and 3 hour tests) for the mechanically activated, non-heat treated serpentine, and the thermally activated, heat treated serpentine. All of the tests on the heat treated serpentine, and the 3 hour test on the attritted serpentine (Table 3, SC-245), were conducted at the following test conditions:  $T=155^{\circ}\text{C}$ ;  $P_{\text{CO}_2}=150$  atm; 15% solids; 0.64 M  $\text{NaHCO}_3$ , 1 M  $\text{NaCl}$ . The 15, 30, and 60 minute tests on the attritted serpentine (Table 3, SC-252, 251, and 250) were conducted at reduced temperature and pressure, with  $T=24^{\circ}\text{C}$  and  $P_{\text{CO}_2}=10$  atm. The extent of the mineral



Table 3.- Summaries for the aqueous mineral carbonation tests conducted on attritted materials.

Test No.	Material	Particle size, $\mu\text{m}^1$	Attrition time, h	Carbonation conditions			Percent stoich. conv.
				Time, min	Temp., $^{\circ}\text{C}$	$\text{P}_{\text{CO}_2}$ , atm	
SC-245 <sup>2</sup>	serpentine	-75	24	180	155	150	81
SC-246	serpentine	-75	24	60	155	150	79
SC-250	serpentine	-75	24	60	24	10	66
SC-251 <sup>3</sup>	serpentine	-75	24	30	25-40	10	65
SC-252	serpentine	-75	24	15	24-40	10	64
SC-253	serpentine	-75	24	15	24	57	58
SC-255	serpentine	-75	24	30	24	10	62
SC-247	olivine	-75	24	60	185	150	91
SC-248	olivine	-75	24	60	24	10	39
SC-256	olivine	-75	5 min	60	185	150	6
SC-257	olivine	-75	1	60	185	150	82
SC-258	olivine	-75	2	60	185	150	81

<sup>1</sup> Particle size of the feed to the attrition machine.

<sup>2</sup> Common test parameters included:

- 0.64 M  $\text{NaHCO}_3$ , 1 M  $\text{NaCl}$  carbonation solution, pH  $\sim 7.8$ , unless otherwise noted;
- 1,000 rpm stirring speed
- 15% solids

<sup>3</sup> Recorded temperature rise to  $40.5^{\circ}\text{C}$  (each ambient temperature test exhibited similar heat up).

dissolution/carbonation reaction was significant within 15 minutes, based on the stoichiometric conversions measured for those tests. The temperature rise observed during all the ambient temperature tests (though only recorded for tests SC-251 and 252)

commenced once the system was purged with  $\text{CO}_2$  and stirring was initiated. Apparently,  $\text{P}_{\text{CO}_2}$  is not as critical for the attritted material, but thorough mixing of the

three-phase system, including gas dispersion, is necessary. This thermal gradient has not been observed during any prior test, and is dramatic evidence of the exothermic carbonation reaction. This suggests that carbonation of the  $\text{Mg}^{2+}$  cations dissolved from the serpentine occurs simultaneously with continued dissolution of the mineral. Carbonate precipitation does not appear to occur exclusively as the system temperature and pressure are reduced, as once postulated. The kinetics of dissolution may be improved further by some increase in reaction temperature above ambient.

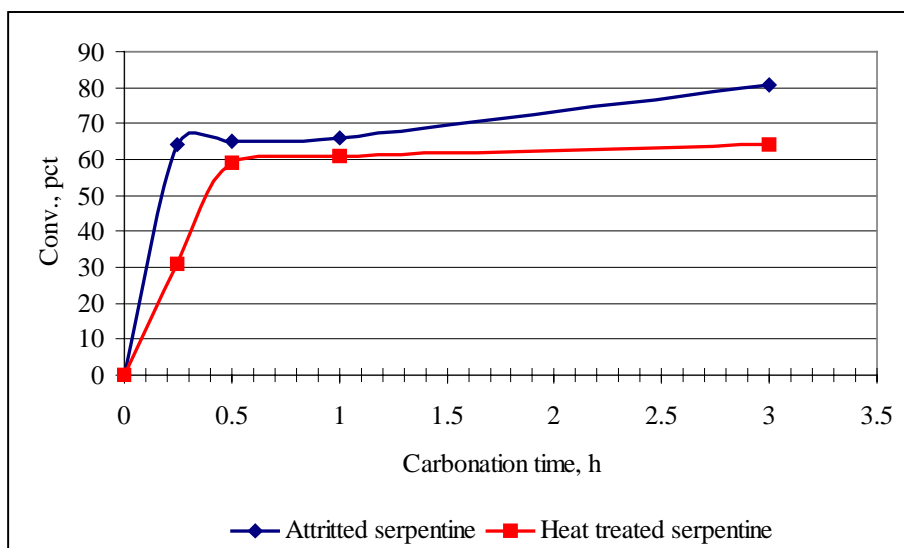


Figure 3.- Carbonation time series for the activated serpentine.

## Olivine Activation

The carbonation time series for olivine included in Figure 4 illustrates the 1-3 hour incubation period prior to significant carbonation. All tests in the time series (0.25, 0.5, 1 and 3 hours), were conducted at the following conditions:  $T=155^{\circ}\text{C}$ ;  $P_{\text{CO}_2}=150\text{ atm}$ ; 15% solids; 0.64 M  $\text{NaHCO}_3$ , 1 M  $\text{NaCl}$ . Chemical activation of the olivine enjoyed limited success, increasing the stoichiometric conversion to the carbonate to ~38% in 1 hour (Table 2, SC-113), under the same conditions. However, the chemical activation pales in comparison to the olivine activation achieved through attrition grinding (Table 3, SC-257), included as a single point in figure 4. Reaction temperature was increased to  $185^{\circ}\text{C}$  for test SC-257, while all other parameters were identical to those used for the time series tests. Stoichiometric conversion (extent of reaction) was increased from ~10% for the non-attritted olivine to over 90% for the olivine attrition ground for 24 hours.

The 24 hour attrition tests were necessary for proof-of-concept purposes. Mechanical activation of the olivine was demonstrated in dramatic fashion, but these long duration attrition times were clearly impractical from a process perspective. Identification of the minimum effective attrition time, and thorough study of that product material, was necessary to determine whether this activation could be achieved by less

energy intensive means, perhaps by modifications to conventional, large-scale grinding mechanisms. Carbonation results for an attrition times series conducted on olivine are included in Figure 5. Carbonation test parameters were held constant for the series, and are included in Table 3. All tests were 1 hour in duration. Attrition times varied from 5 minutes to 24 hours.

The results from the olivine attrition time series are encouraging. Tremendous activation of the olivine was achieved with the addition of a 1 hour attrition step. Although the 5 minute attrition time appeared ineffective, carbonation in excess of 80% of the stoichiometric maximum was achieved in 1 hour using olivine attrition ground for 1 hour. Thus, attrition times exceeding 1 hour do not appear necessary. The samples of the attrition products are currently undergoing analyses for specific surface area, particle size, and phase determination by XRD. The results

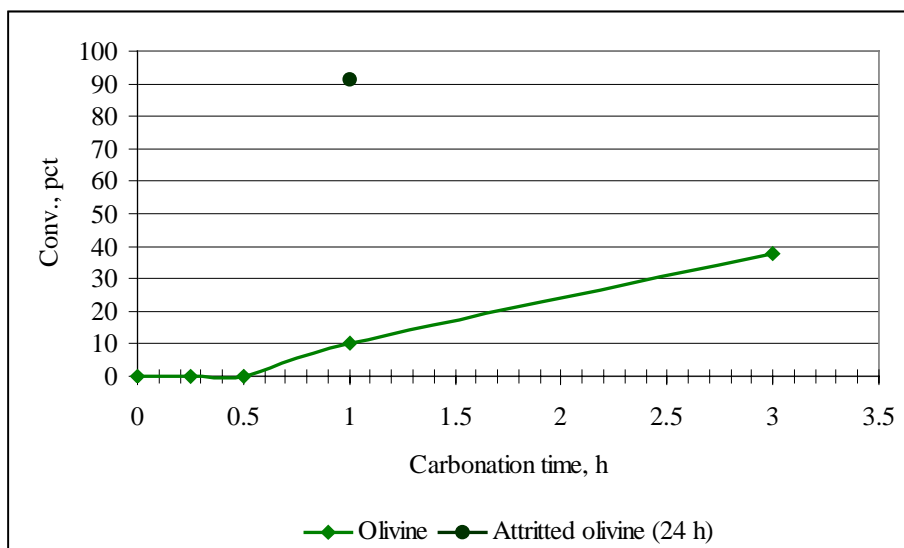


Figure 4.- Carbonation time series for olivine (single point for attritted olivine).

from these analyses should lead to a better understanding of the activated olivine, which may become the standard for evaluation of other mechanical activation techniques, and to which other mechanically activated materials will be compared. A similar attrition time series for serpentine is in process.

The attrition studies conducted to date have demonstrated that carbonation reaction times

can be dramatically reduced by mechanical activation. In addition, these reduced reaction times may be accompanied by significant reductions in the carbonation process parameters.

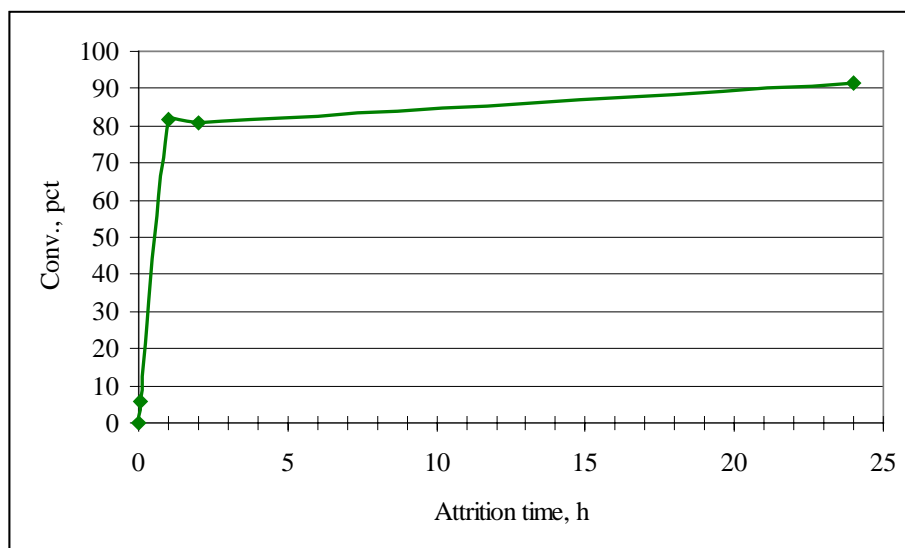


Figure 5.- Carbonation results for the olivine attrition time series.

## Conclusions

Conclusions based on the most recent experimental studies include the following:

1. Mechanical activation of serpentine and olivine can be achieved by the addition of an attrition grinding step to the grinding circuit. Attrition grinding appears to destroy the crystal structure of either mineral, creating an amorphous phase, based on preliminary XRD results.
2. Carbonation results for an attrition time series conducted on olivine indicate that attrition times exceeding 1 hour are not necessary.
3. Carbonation reaction times have been reduced to 1 hour or less for the mechanically activated minerals. Carbonation reaction parameters can also be reduced significantly, to  $T=25^{\circ}\text{C}$  and  $P_{\text{CO}_2} \sim 10$  atm, while still resulting in carbonation up to 65% in 1 hour.
4. Dehydroxylation of serpentine is not necessary for carbonation. Mechanically activated serpentine retains the chemically-bound water (hydroxyl groups), based on the LOI of the attrition product. The chemically-bound water does not appear to inhibit carbonation.

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