

Factors Affecting Ex-Situ Aqueous Mineral Carbonation Using Calcium and Magnesium Silicate Minerals

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Carbonation of magnesium- and calcium-silicate minerals to form their respective carbonates is one method to sequester carbon dioxide. Process development studies have identified reactor design as a key component affecting both the capital and operating costs of ex-situ mineral sequestration. Results from mineral carbonation studies conducted in a batch autoclave were utilized to design and construct a unique continuous pipe reactor with 100% recycle (flow-loop reactor). Results from the flow-loop reactor are consistent with batch autoclave tests, and are being used to derive engineering data necessary to design a bench-scale continuous pipeline reactor.

INTRODUCTION

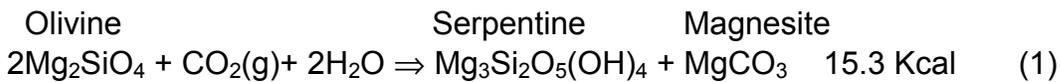
There is a growing body of evidence that the earth's climate is warming. The Intergovernmental Panel on Climate Change (IPCC) estimates that the average global surface temperature of the Earth has increased by $0.6 \pm 0.15^\circ\text{C}$ since the late 19th century. The 1990s were the warmest decade on record, and 1998 was the warmest year in the instrumental record. During this same period the Arctic growing season increased, Alaskan glaciers retreated and the sea level rose an estimated 1.5 mm/year. The cairns marking the retreat of the Athabaska Glacier in Jasper National Park are a graphic illustration that the glacier is shrinking.

At the same time, the concentration of carbon dioxide in the atmosphere has been increasing. Carbon dioxide is a greenhouse gas, and there is growing evidence and theory that the increase in the Earth's surface temperature and the increase in CO₂ concentration are causally related. Because global warming could lead to many environmentally devastating consequences, such as more frequent and intense storms, higher maximum temperatures over all landmasses, and increased continental drought, there have been international calls for the reduction of CO₂ emissions.

Fossil-fuel-fired power plants account for approximately one-third of the total CO₂ emissions. Because burning carbon in air must yield CO₂, it is impossible to modify fossil-fuel-fired power plants to stop producing CO₂. Therefore, if CO₂ emissions from fossil-fuel-fired power plants are to be reduced, either the plant must be made more efficient, or the CO₂ must be captured and stored. Proposed methods to sequester CO₂ include terrestrial and ocean sequestration, geological sequestration, and mineral carbonation. Of these, mineral carbonation has the greatest promise to provide the stability required for long-term storage, albeit at a significant energy and economic cost (O'Connor *et al.* 2004).

The U. S. Department of Energy's Albany Research Center carbon-sequestration program includes both in-situ (Rush *et al.*) and ex-situ elements. The ex-situ work has focused on accelerating naturally occurring carbonation reactions enough that they could economically be carried out in a traditional chemical plant. The reaction rate is accelerated by raising the activity of CO₂ in solution, heat (but not too much), reducing the particle size, high-intensity grinding to disrupt the crystal structure, and, in the case of serpentine, heat treatment to remove the chemically bound water. All of these carry energy and economic penalties.

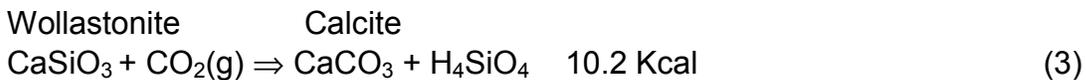
Magnesium-, calcium- and iron-silicate minerals react with CO₂ to form geologically stable carbonates via chemical reactions 1-4.



By increasing the CO₂ activity it is possible to form magnesite and no serpentine (eq 2).



It is also possible to form calcite and siderite by similar reactions (eq. 3 and 4).



Several important conclusions can be drawn from these equations. All of the reactants and products of these reactions (olivine, serpentine, magnesite, wollastonite and calcite) can be found in significant quantities in nature and thus, under the proper conditions, are stable for geologic periods of time. The reaction products, magnesite, serpentine, calcite, and siderite, are at a lower thermodynamic state than the reactants. Thus over geologic time, olivine is eventually converted into serpentine and magnesite, making serpentine more prevalent than olivine. Once magnesite has formed, CO₂ can be stored indefinitely. Finally these are geologic reactions and have geologic reaction rates. The challenge is to accelerate these reactions several orders of magnitude so that it is possible to carry them out in a chemical plant at minimal cost of capital and energy.

Thermodynamically these are interesting reactions. Figure 1 is an equilibrium composition calculation using HSC Chemistry for Windows. At atmospheric pressure, depending on the temperature, 6 different species can occur: carbonates (2 hydrated forms and one non-hydrate), silicates (both olivine and

serpentine), and magnesium oxide. Below 50°C hydromagnesites [$\text{MgCO}_3(\text{H}_2\text{O})_5$ and $\text{MgCO}_3(\text{H}_2\text{O})_3$] are the major species. Raising the temperature increases the amount of non-hydrated magnesite. Above about 125°C magnesite begins to decline and some serpentine appears. As the temperature rises above 200°C olivine and MgO are formed. Raising the pressure extends the region of magnesite stability and suppresses the formation of serpentine and MgO. At 150 atmospheres of CO_2 , where most of the test work was done, only magnesite is seen to any appreciable extent. Below 100°C, the two hydrated forms of magnesite are stable, and above 100°C only non-hydrated magnesite occurs. This is consistent with experimental results. Hydromagnesite was detected only (by X-ray diffraction) only when serpentine was made extremely reactive by attriting the mineral long enough to destroy the crystal structure, making it possible to get substantial carbonation at room temperature.

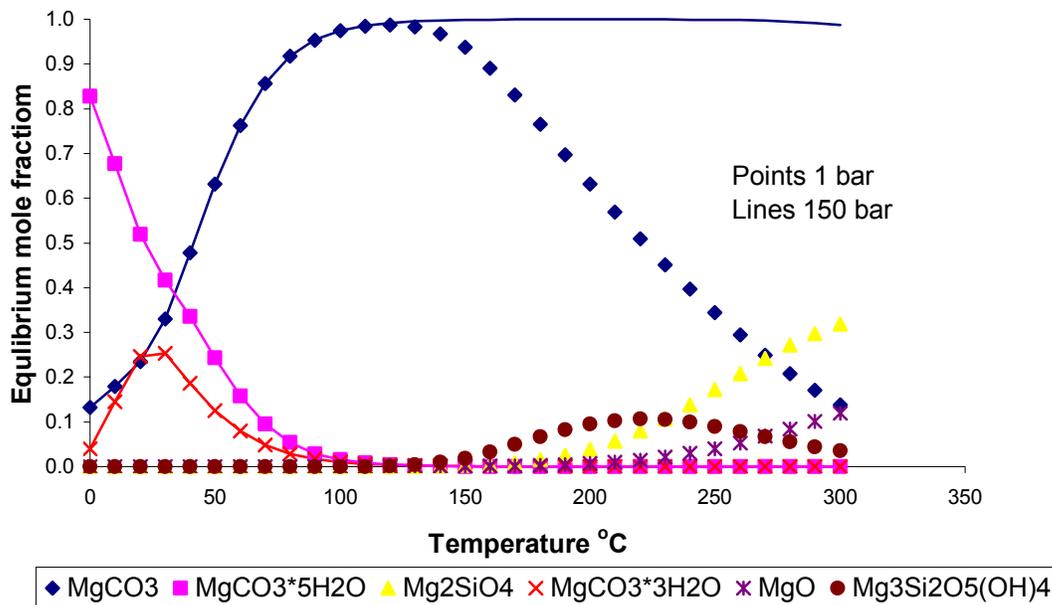


Figure 1. Equilibrium thermodynamic calculation of the Mg_2SiO_4 - CO_2 - H_2O system.

BATCH AUTOCLAVE RESULTS

Magnesium-silicate and calcium-silicate minerals were chosen for study because of their abundance and occurrence near coal-fired power plants in the Northwest, the Northeast and Texas (O'Connor *et al.*, 2004). Specific minerals studied were Southwest Oregon lizardite (serpentine), Cedar Hill antigorite (serpentine), Twin Sisters olivine and Nyco wollastonite. Head analyses of the mineral reactants are shown in table 1. The lower Mg concentration in the serpentine minerals is due to the presence of ~14 wt pct chemically bound water. R_{CO_2} represents the ratio of

the mass of ore required to carbonate one unit mass of CO₂, assuming 100% conversion of Fe⁺², Mg and Ca cations available in the mineral. The lower R_{CO₂} (~1.6) for olivine as opposed to serpentine (2.2) means considerably more serpentine would have to be mined to sequester the same amount of CO₂, and more yet for the wollastonite (R_{CO₂} ~2.7). The Twin Sisters olivine deposit in northwest Washington State is estimated to contain over 2 billion tons of ore, enough to carbonate all of the CO₂ emissions from 8-10 1-GW coal-fired power plants for ~15 years. Enough serpentine exists in massive ultramafic sequences to sequester all of the CO₂ produced from all coal resources.

Table 1. Head analyses.

	Serpentine antigorite	Serpentine lizardite	Olivine	Wollastonite
	%	%	%	%
Ca	0.019	0.314	.0112	32.9
Fe ⁺²	2.61	2.40	6.0	0.53
Fe ⁺³	1.29	2.02	<.01	.001
Mg	26.1	23.9	31.1	0.274
Si	17.3	18.0	18.9	22.7
Water ¹	0.440	1.59	0.070	0.05
LOI ²	15.1	14.8	0.390	3.23
R _{CO₂} ³	2.03	2.12	1.64	2.70

1 - Free moisture, measured as the weight loss after 1 hour at 105°C, in air.

2 - Loss on Ignition, measured as the weight loss after 1 hour at 1000°C, in argon.

3 - Ratio of ore mass that must be processed to carbonate 1 unit mass of CO₂, assuming 100% carbonation of all Ca, Fe⁺², and Mg.

The magnesium-silicate mineral reactions were carried out in an aqueous solution of 0.64M NaHCO₃, 1M NaCl in a batch autoclave. The 0.64M NaHCO₃ solution concentration is the solubility limit of the bicarbonate at room temperature. This bicarbonate solution was found to significantly improve the reaction rate for magnesium-silicate minerals by increasing the activity of the carbonate in solution. The rate of carbonation of the calcium-silicate mineral, wollastonite, was not increased as much by the carbonate solution and therefore most wollastonite experiments were carried out in distilled water.

Figure 2 shows the batch autoclave results for serpentine, olivine, and wollastonite carbonation experiments in a batch autoclave. With serpentine, the reaction rate is quite slow unless the chemically bound water is removed by heat treatment. Unfortunately this carries a substantial energy penalty, approximately 290 kW•h/ton for antigorite and 325 kW•h/ton for lizardite (O'Connor *et al.*, 2004). It is possible to obtain similar results with very intensive grinding, however this carries a similar energy penalty. Heat-treated serpentine reacts rapidly, reaching an extent of reaction of 50% in an hour but the maximum never exceeds 65%. Olivine carbonation proceeds to over 80% carbonation in 6 hours. However, for shorter periods of time the extent of reaction is less than heat-treated serpentine. At one hour the extent of reaction is similar to that of heat-treated serpentine. Wollastonite is the most reactive, reaching over 70% in less

than an hour, and unlike the magnesium minerals the wollastonite reaction proceeds rapidly in distilled water.

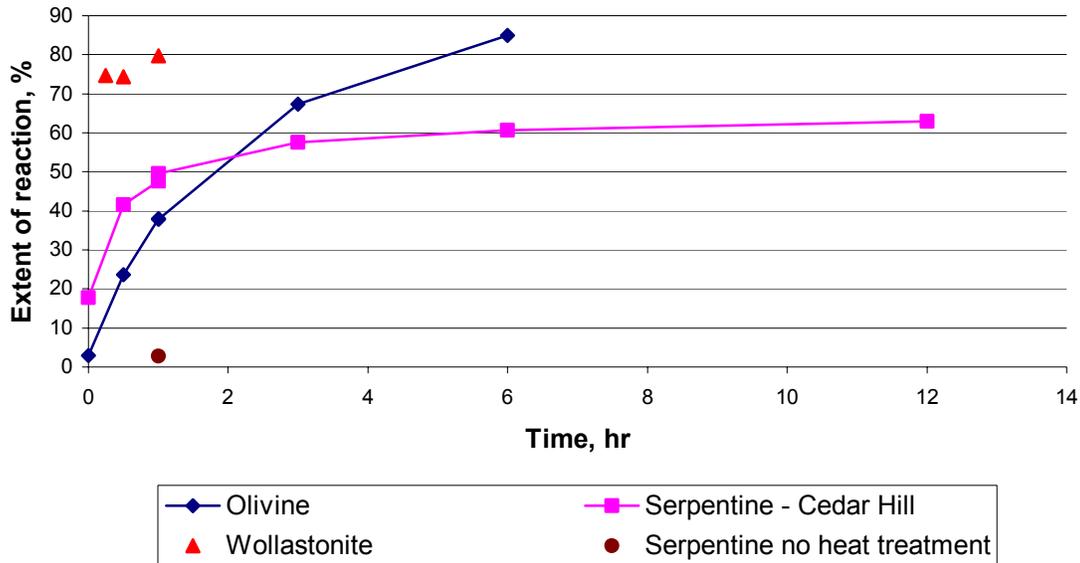


Figure 2. Extraction at 185°C and 150 atmospheres CO₂

For olivine, wollastonite and heat-treated serpentine the most effect way to accelerate the reaction is to increase the surface area by decreasing the particle size. The work index to grind to 200 mesh (75 μm) was estimated to be 11 kW•h/ton. However, with 200 mesh-particles the extent of reaction is only 14% in one hour or 52 in 3 hours. Previous work has shown that high-energy attrition grinding can significantly increase this reaction rate. The attrition mill used is a chamber filled with 3mm stainless-steel balls are stirred at 300 rpm by a shaft with 3 pins mounted such that the top and bottom impellers are parallel with the middle but offset at 90°. One hour in the attrition mill reduces particle size to ~ 50% minus 2 to 4 μm (D_{50}) depending on whether the mill is run wet or dry. Wet milling results in smaller particles, but under the right conditions, dry milling can produce non-crystalline material that is significantly more reactive. Unfortunately, attrition-grinding is more energy-intensive than conventional grinding and may not be scaleable to the size required for carbon sequestration.

When the shrinking-particle model holds, the surface area, and thus the particle size, has a significant impact on the reaction rate (Ityokumbul *et al.*, 2001; Gerdemann *et al.*, 2003). Previous work by O'Connor *et al.* (2000, 2002) found large unreacted olivine particles and small particles (~10 μm) of magnesium-carbonate product. No variation of magnesium content was seen from the surface to the center of the larger particles. This is consistent with the particle surface reacting to release magnesium into solution and then precipitation of small magnesium-carbonate particles from the solution. Experiments with wollastonite are also consistent with the shrinking-particle model.

Because the reaction rate is sensitive to the particle size, which is determined largely by feed preparation, it is difficult to compare test series with differently prepared feed. For this reason and to make comparisons easier, the extent of reaction in one hour was normalized. The extent of reaction in one hour for a particular test was divided by the maximum extent of reaction in one hour for that particular material. Figure 3 shows the effect of raising the reaction temperature from room temperature to 250°C on the extent of reaction. For Twin Sisters olivine, the maximum extent of reaction in one hour (50%) occurred at 185°C. Two factors work against raising the temperature: (1) CO₂ activity in solution decreases, and (2) the reaction becomes thermodynamically less favorable. Thus, above some temperature, the extent of reaction decreases. This temperature is approximately 185°C for olivine and 155°C for heat-treated serpentine. Wollastonite has a broad peak beginning at 100°C.

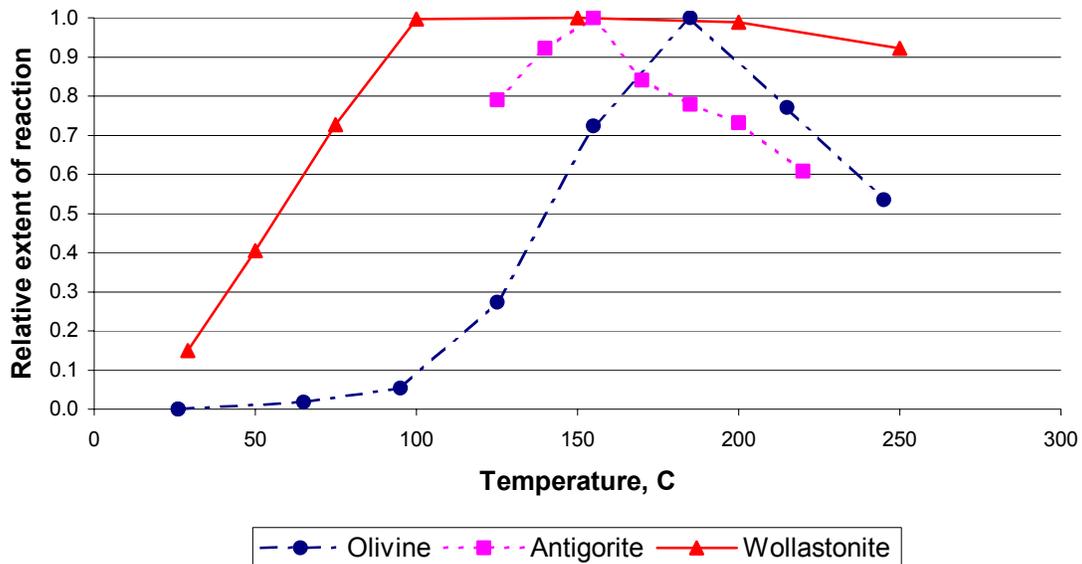


Figure 3. Effect of raising the reaction temperature

Raising the partial pressure of CO₂ also increases the extent of reaction in one hour (figure 4). This is due to the increased activity of CO₂, and pressure also pushes the reaction towards completion because the volume changes due to the conversion of CO₂(g) into solid MgCO₃.

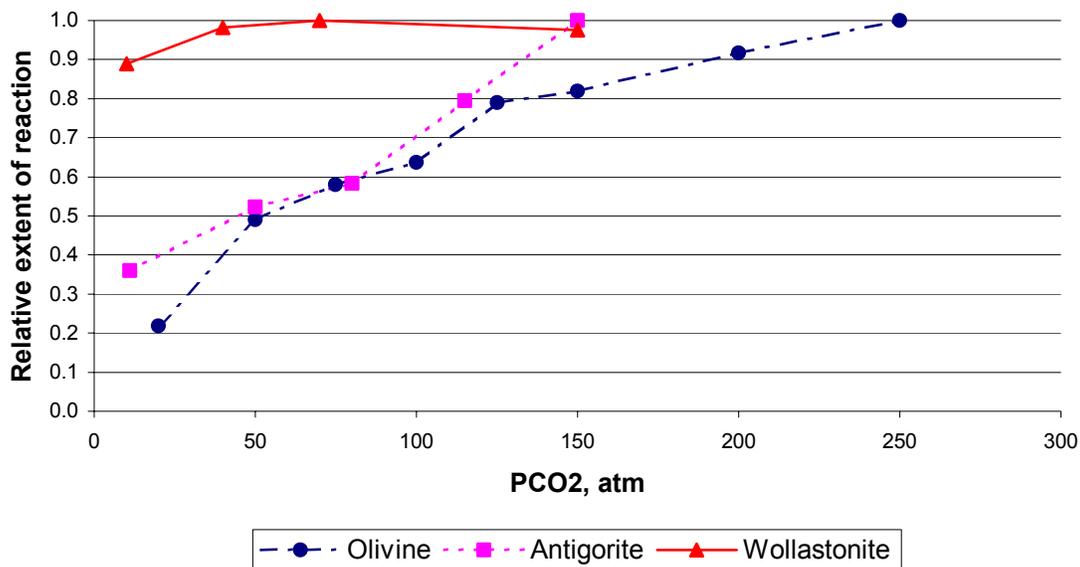


Figure 4. Effect of raising the partial pressure of CO₂ at 185 °C.

THE FLOW-LOOP REACTOR

The Coal Utilization Science (CUS) group at the Department of Energy's National Energy Technology Laboratory (NETL) did a cost evaluation of mineral carbonation of olivine based on a compilation of proposed materials and operating parameters supplied by ARC. The results from this study show the continuous-flow autoclave reactor as the largest capital-cost item. The reactor alone constitutes 2/3 of the plant cost. An alternative design such as a plug-flow reactor (Penner *et al.*, 2003 a,b) should result in substantial cost savings for the process.

Although slurry flow through and reaction in pipes are not new ideas, the high-temperature, high-pressure, three-phase conditions required for optimum mineral carbonation are unusual. Hence, information on viscosity, density, cavitation, and wear and corrosion data are unavailable for the anticipated conditions. To obtain these data in a continuous plug-flow reactor of sufficient length to get the required residence time (estimated to be a minimum of 15 minutes) at flow rates that would keep the slurry suspended and the gas well mixed would be expensive, difficult, and require a substantial amount of feed material. For this reason, a research reactor was designed and constructed that includes the elements of pumping and flow through pipe, but without the high material and reactant costs of a continuous system. This reactor – the flow-loop reactor - is a plug-flow reactor that achieves residence time by recirculating the reactants through a loop many times, essentially a plug-flow reactor with 100% recycle. Using this reactor it is possible to generate some of the important engineering data needed for a continuous system at reasonable expense. Results of the autoclave experiments were used to design this reactor. Design and construction, as well as some results, are described in Gerdemann (2003) and

Penner *et al.* (2003 a,b). This first prototype reactor was called the high-temperature, high-pressure (HTHP) flow-loop reactor.

Figure 5 is a conceptualized drawing of the reactor and figure 6 is a photograph of the actual reactor before insulation was added. The drawing accurately depicts the placement of all the relevant parts of the reactor seen in the photograph. In order to keep the cost down and minimize the amount of feed preparation, the reactor was built using the smallest practical pipe size. The smallest manufacturer-recommended static mixer available was designed to fit into $\frac{1}{2}$ " ID flanged 300 series stainless steel pipe. This pipe is rated to handle the high pressure (2300 psig) and high temperature (185°C) necessary for the reaction. This set the size of the reactor. The system was designed with flanged tees and crosses in the pipe at strategic points that allow insertion of thermocouples into the slurry flow to control and measure temperature. The flanged construction improves the safety of the system but increases the heat requirements due to its large mass and constricted areas for attachments to the apparatus such as heaters and monitoring probes. System pressure is controlled and monitored at the top of the system. CO₂ is injected in two different places. Differential pressures are similarly monitored at tees and crosses on each side of mixer pairs and at points on opposite sides of the pump to measure total pressure drop across the pump. Also located after each mixer pair is a threaded cross fitting with a view port. These are the only places operators can actually see into the reactor to help with filling, draining, and physically viewing the mixed reactor contents. Unfortunately, once slurry flow is established the contents are no longer visible.

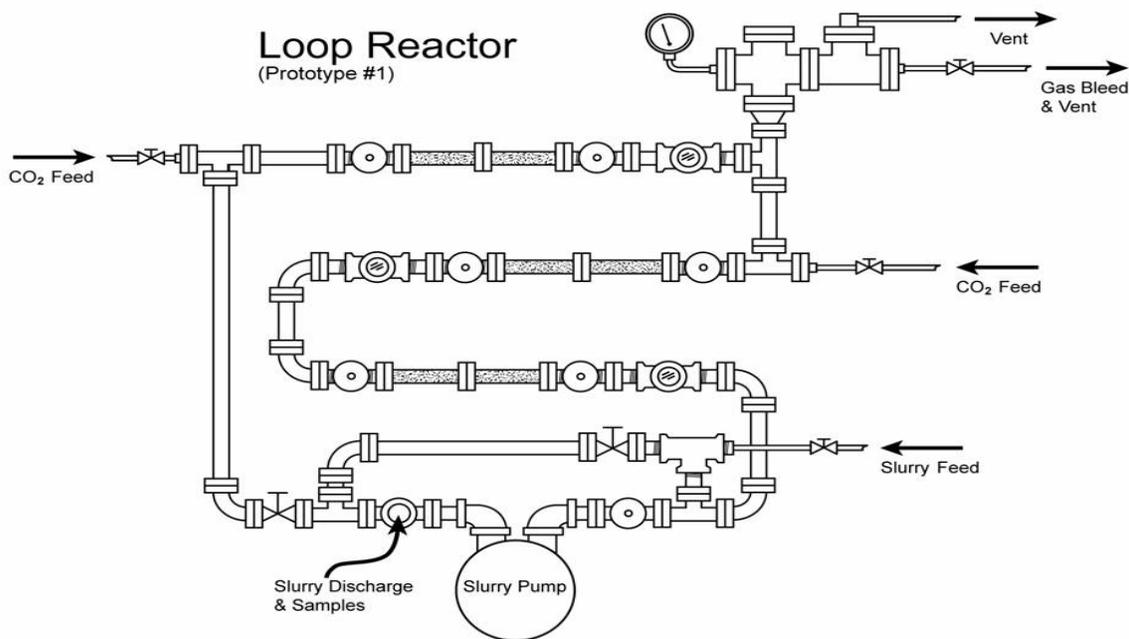


Figure 5. Conceptualized model of the flow-loop reactor.

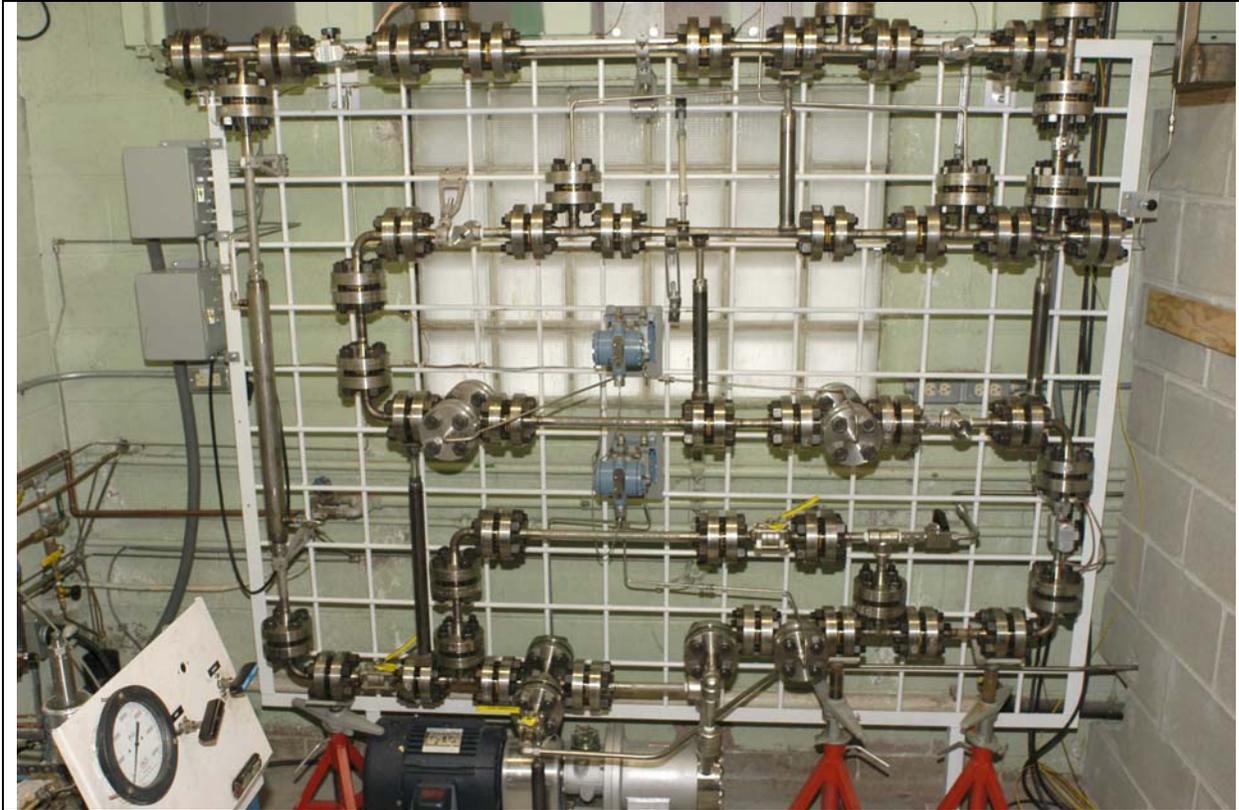


Figure 6. Completed Prototype #1 HTHP Flow Loop Reactor. Mounting rack is 7' wide and 5.5' high.

RESULTS OF FLOW-LOOP REACTOR OPERATION

Reactor tests were designed to correlate with the large body of work done in batch autoclave tests that were used to optimize feedstocks and test parameters. Slurry composition consists of finely ground olivine suspended in bicarbonate/saline carrier solution ($0.64\text{M NaHCO}_3 + 1\text{M NaCl}$). A typical test starts with purging the reactor with CO_2 for about a minute, followed by pumping pre-mixed slurry of known slurry density (usually 15 wt %) into the reactor. The system pump is operated at 1200 rpm to recirculate the slurry continuously through the reactor, and enough CO_2 is injected to reach a pressure of 150 psi. This is enough pressure to prevent steam problems during heat-up, but not enough for significant carbonation reaction. As soon as the reactor reaches 185°C (approximately 3 hours), the remaining CO_2 is added to reach operating pressure of 2375 psi; this value reflects the partial pressure of steam plus 2200 psi (150 atm) partial pressure of CO_2 .

To compare the reactor efficiency for a highly activated feed (olivine ground with a high-intensity attritor to $D_{50} = 4\ \mu\text{m}$), the same material was carbonated using the same test conditions in the batch autoclave. The extent of carbonation was 72%, the same value found for the flow-loop test at 1.8 L fill volume.

A coarser feed (Table 2) was also tested in the flow reactor. This minus 400-mesh ($D_{50} = 14 \mu\text{m}$) olivine feed had been resistant to reaction in the autoclave, consistently reacting to less than 10% of its theoretical extent in one hour at the normal HTHP conditions. This material may have been passivated for carbonation due to lengthy storage in water after initial grinding. When processed in the flow reactor, however, this material attained about 70% extent of reaction. A duplicate test was run in the flow-loop reactor and similar results were obtained, for an average of 72% for the two runs. To see whether the longer warm-up time for the flow-loop reactor is a factor, a longer warm-up time was used in the autoclave as well, but no significant increase in the reaction rate was measured.

Table 2. Carbonation results in the flow-loop reactor

Pump Speed	Size	Extent of reaction ¹
RPM	Mesh	%
1198	-400	72.0
1750	-200	77.9
1450	-200	73.8
1198	-200	63.2
1002	-200	66.9
No Mixers		
1198	-200	37.5
1002	-200	47.1

1- For Comparison the extent of reaction for the same the same -400 mesh material was 4.2%.

This raises an interesting question: what causes the coarser feed to be so much more reactive in the flow-loop reactor than in the autoclave? There is probably more turbulence in the loop reactor. Other work has shown that the reaction starts with Mg ions being dissolved into the carrier solution and then precipitated as carbonates on the particle surface. Both the product and the silica deposits left behind may hinder further Mg dissolution. In the turbulent environment of the flow-loop reactor, the high-energy particle-to-particle interactions may remove surface oxidation and reaction products and expose fresh surfaces to further Mg dissolution and reaction. This is consistent with results from the batch autoclave work, which indicate that the reaction follows the shrinking-particle model.

If the flow-loop conditions create fresh reaction surfaces, is it happening in the pump, in the mixer zones or in the straight sections of the pipe? Future tests are planned with fewer mixers that should help answer these questions. Tests at higher pump speeds show only a marginal increase in reaction rate. When the stir rate was too low in the batch-autoclave tests, the reaction rate dropped dramatically, indicating poor gas/liquid mixing. This was confirmed visually in a transparent mock-up of the autoclave. Below 1000 rpm there is no gas infusion into the liquid and the reaction does not proceed to any appreciable extent. When the minimum stirring was reached, further increases had little effect. The small increase in reaction rate in

the flow-loop reactor when the pump speed is increased is probably from increased wear on the particle surface and not from improved gas/fluid mixing.

CONCLUSIONS

Mineral carbonation experiments have been conducted on three different silicate minerals with the goal of forming carbonates for CO₂ sequestration. The reactivity of the minerals is inversely related to their relative abundance. Serpentine (hydrated magnesium silicate) is the most abundant and the least reactive. Only energy-intensive steps such as heat treatment or high-energy grinding make it possible to carbonate serpentine. Olivine is less abundant than serpentine. The extent of carbonation in one hour varies from near 0 to over 90% depending on the particle size and temperature and pressure at which the reaction takes place. Wollastonite is the least abundant of the minerals used in this work, although the exact abundance is unknown. It is possible to achieve 70% carbonation of wollastonite in one hour in distilled water at lower pressure and temperature than is required to achieve the same results for olivine.

A unique continuous high-temperature and high-pressure slurry flow-loop reactor has been designed and operated. This loop reactor is a continuous plug-flow reactor with 100% recycle that can handle a gas/liquid/solid slurry at over 200°C and 2500 psi. Carbonation reaction rates are similar to those achieved in a stirred autoclave for highly ground feedstock, but much improved reactivity is achieved in the flow-loop-reactor with coarser mineral feed.

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