Modeling Flow of Mineralized Carbon Dioxide Slurry

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Abstract

Direct mineral carbonation was investigated at Albany Research Center (US DOE) as a means to sequester carbon dioxide into stable mineral matrices. Although previous work focused on treating Mg-containing minerals in conventional autoclaves, recent work has been done using pipeline-reactor technology for the high-temperature, high-pressure (HTHP) reaction of the minerals in aqueous/CO_2 media. Sequestration of CO_2 using above-ground reactors may be uneconomical, but the technology may also be applicable in geological sequestration of CO_2. Progress is described in using a prototype HTHP flow-loop reactor to model flow in the dynamic three-phase system to help determine the pumping-energy requirements to optimize reactivity.

Introduction

Because of the stability of its mineral form, one of the most promising ways of sequestering carbon dioxide (CO_2), and thus mitigating its potential impact on global climate, is to cause CO_2 to react with mineral silicates to form carbonates. Large Mg-, Fe-, and Ca silicate deposits, more than sufficient for the world's fossil resources, are available as chemical precursors for carbonate formation. These chemical reactions are a normal part of the carbon cycle, but the natural global reaction rates are unable to keep pace with the world's current output primarily from the combustion of fuels for energy production. To prevent the continued buildup of CO_2 as a climate-altering greenhouse gas, the technological challenge is to accelerate reaction rates to economically acceptable time frames that could result in a cost-effective carbon sequestration process.

Albany Research Center (ARC, U.S. Department of Energy) is investigating carbon mineralization strategies for safe sequestration of CO_2. The first several years of research focused on understanding CO_2 mineralization reactions and optimizing several parameters to improve reaction rates. A comprehensive overview has been recently made available by O'Connor et al. (2005). The process developed by this effort is known as direct mineral carbonation. The method treats the reactant, olivine or serpentine, in aqueous media with carbon dioxide at high temperature and pressure to form the mineral carbonates.

To determine the costs of sequestering CO_2 using this process, a compilation was made at ARC (Nilsen and Penner, 2001) of proposed materials and operating parameters to be used for a cost study funded by the Coal Utilization Science (CUS) program at DOE's National Energy Technology Laboratory. The following summarizes the process in a hypothetical plant for cost evaluation.

In the process, olivine would be transported from an open-pit mine in the Twin Sisters area of Washington State to the site of the sequestration plant located nearby. Carbon dioxide would be piped from a nearby coal-fired power plant. The sequestration plant would process about 24,000 metric tons per day of CO_2 using 55,000 metric tons per day of olivine. The olivine

would be ground and slurried with carrier solution (0.64M NaHCO$_3$ and 1M NaCl) and contacted with supercritical CO$_2$ in conventional continuous-flow autoclaves at 2300 psig and 185º C for two hours. The mineral carbonate slurry product would be cooled and filtered, and unreacted mineral would be separated and recycled with carrier solution. The carbonated mineral product would be finally sequestered at the mine.

In the draft report by Lyons et al. (2003), some useful information was provided about the process. The largest capital-cost item is the reactor. In the example described above, a train of large expensive autoclaves for the reaction constitutes 2/3 of the plant cost. Clearly, reactor design is an important place to start cutting costs for the process. The other significant way to cut costs is to speed up the reaction to much less than two hours.

The study concluded that the expected costs of sequestering CO$_2$ would be about $69 per ton of CO$_2$, a cost that is much higher than the $10 per ton that was a goal of the research. Since then, the research has evolved into two separate areas. In the first, the insights learned would be applied to geological sequestration both by better understanding the mineral trapping potential underground and by applying mineral carbonation techniques to capping or sealing underground CO$_2$ reservoirs.

The second area of study, the area of focus for this paper, involves cutting the cost of mineral carbonation by improving the reactor technology. A general rule for construction of large pressure vessels is that wall thickness of a pressure vessel is directly related to its diameter, and cost of such a vessel is directly related to its wall thickness. These considerations lead to the conclusion that substantially lower costs could result from a pressure vessel design change. The improved reactor would have a smaller diameter and corresponding wall thickness. One possible modified reactor design is a pipeline reactor. A continuous version would use mineral slurry and pressurized CO$_2$ injection into a heated pipe of sufficient length for optimized extent of reaction. The reacted product would be removed at the other end of the pipeline and treated as previously described. The work described in this section is in support of this concept. If direct mineral carbonation is to be a viable option for CO$_2$ sequestration, an inexpensive continuous reactor such as the pipeline concept reactor must be developed.

We previously reported that ARC has developed a research reactor to study mineral carbonation (Penner, *et al*. 2003 a,b). In those reports we described the technical challenges that need to be met to move ahead in this research. The first challenge is to accurately measure flow under the extreme conditions in the reactor, and the second is to improve the reaction rates to lower costs. Both of these subjects are discussed in this paper.

The challenges of flow measurement

The simplest way of measuring flow of multiphase fluids through pipes is to catch fluids at the terminal end and measure each phase as it passes. For research purposes, such a system would have very large materials and structural requirements. The minimum size of a pipeline long enough to drive the reaction more than half way to its theoretical maximum extent may be on the order of 1 kilometer. We estimate that several slurry pumps would be required at intervals to keep the slurry moving through the pipe at a sufficient rate for effective transport and reactivity. The heating, insulating, and other infrastructural requirements would also be large. Even short intervals of operation would require large quantities of finely-ground ore and chemical components for the reaction. To keep costs of this research manageable, a prototype high-temperature, high-pressure (HTHP) flow-loop reactor was designed and constructed. Its most current form is shown in figure 1.

Because it is a batch reactor, the flow-loop reactor cannot be monitored for flow at HTHP conditions by catching the slurry. Indirect means of flow measurement are necessary. Flow rates
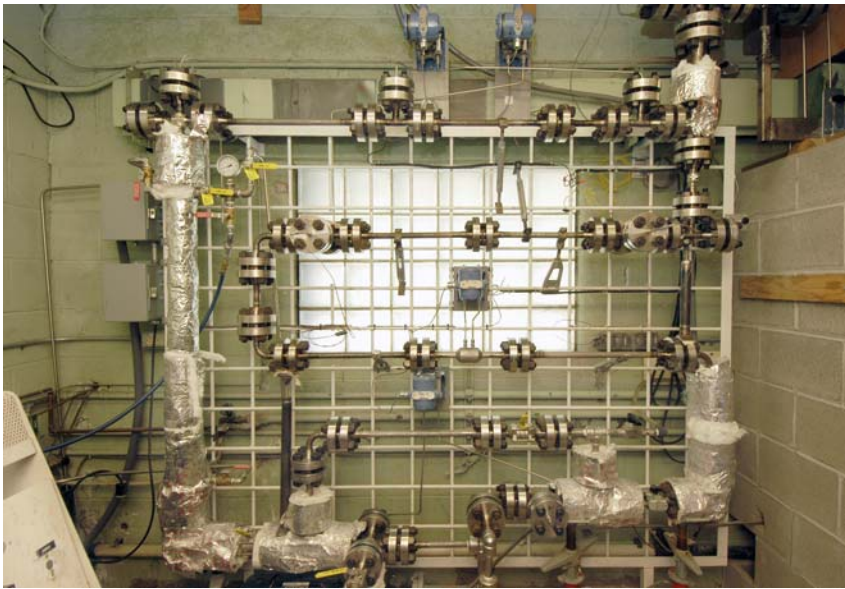
Figure 1 - HTHP flow-loop reactor.

are difficult to measure in the hostile environment inside the reactor. Flow meters with moving parts such as paddle wheels were avoided because of the HTHP conditions. Doppler-type flow meters were initially chosen because the flow transducers clamp onto the outside of the pipe thereby avoiding attack and degradation from contact with reaction slurry. The reactor was fitted with two types, one that is preferred for no- or low-solids flow, and the other for high-solids flow. Neither proved effective for the system due to a combination of electrical and sonic interferences, phase and flow character changes, and other unresolved problems.

Another type of flow meter that is widely used for slurries is known as the Coriolis mass flowmeter. This type of meter was not selected for the HTHP flow-loop reactor, however, because it is reported to be unable to accurately and consistently measure two-phase flow and aerated liquids (Reizner, 2004).

Electromagnetic flow meters are typically used to measure fluid velocity in pipes. They measure the voltage that is induced when conductive fluids move through the meter's magnetic fields. The electrode voltage is directly proportional to the average fluid velocity. They also require a separate measurement of density or phase holdup. Although we were unable to procure any meters of this type that would perform at the HTHP conditions required for the reaction, we obtained an electromagnetic meter to help calibrate multiphase flow at low temperature and pressure.

Horizontal flow measurement, as in the flow-loop reactor, is difficult because density stratifications occur (Oddie and Pearson, 2004). Global measurements will not suffice unless there is a deliberate attempt to mix the phases either with static mixers or a device that will condition flow near the measurement of pressure drop. For this set of tests we decided to install a pressure-drop meter with a V-cone that conditions flow while measuring pressure drop. Before testing at HTHP, a series of calibrations were run using this meter and the electromagnetic meter (figure 2).

Calibrating pressure-drop flow measurement

To accurately calibrate the reactor at ambient conditions, the reactor was modified to allow surge collection of fluids, and thus, allow capture and measurement of timed batches. A stirred surge tank that contained measured quantities of carrier solution and solids was attached to a rack that allowed the slurry to be fed through a funnel and short tube to the primary slurry pump. After circulating through the reactor, the slurry exited back into the surge tank. The exit flow was easily diverted to a bucket for timed periods, usually 20 or 30 seconds.

Figure 2 - V-cone flow tube (left) and electromagnetic flowmeter (right).

The collected slurry was measured for volume and weight, and flow rate was calculated for both mass and volume with these measurements. By adding more solids, calibrations were extended to progressively higher slurry densities. The reactor was calibrated using 5 static mixers that promote aggressive mixing. Due to the dense mixing element design, substantial pressure drop occurs across these mixers, and flow rates are limited to about 3 gallons per minute (gpm) for this reactor configuration. We previously reported (Penner et al., 2004) that this type of mixer readily clogs with solids during carbonation tests, so we were careful to clean them after each calibration test and after each carbonation test. After these calibration tests the mixers were removed and replaced with a simpler spiral design. The spiral mixer is much less efficient at mixing the phases but is less prone to clogging. For equivalent pumping speeds, the flow rates achieved with three of these mixers in the reactor were about double the rates achieved with the first series of mixers. See figure 3 for a picture of the two mixer types.

Figure 3 - Static mixers: high-mixing design (top) and spiral mixer (bottom).

During calibration tests, the output from the V-cone pressure-drop meter was fairly stable as long as the injection of CO_2 was sufficiently low to keep the flow regime in a bubble-flow mode. When the injection rates were increased to cause slug formation in the pipe, the pressure-drop measurements exhibited high instability. The meter uses a relationship between pressure-drop and flow as shown in equation 1

$$F = k\sqrt{\Delta P} \qquad \text{(Eq. 1)}$$

where F is the flow rate in gallons per minute, ΔP is the pressure drop across the flow meter, and k is a constant that is found by calibrating for a given fluid's flow characteristics. Effective range for the meter is between 1 and 10 gpm.

Although the meter is supplied with a calibrated value for k, the complexity of the multiphase conditions in the pipe required a calibration that used the olivine slurry in carrier solution. Calibration runs using the mixers shown at the top of figure 3 revealed that the square root of the meter's output was not quite linear, but a good estimate for k was 5.5 in the flow range for carbonation tests using 1.6L fill volumes and about 5.8 for carbonation tests with 1.8L fill volumes. This first value holds for ambient conditions with an estimated 90 volume% slurry and 10 volume% CO_2 in the case of the 1.6L fill, and approaching 0% CO_2 in the case of 1.8L fill volume. Modeling flow by a computer fluid dynamics program has begun at the Computational Fluid Dynamics Laboratory, but the model is still being adapted to better predict flow as temperature and pressure rise in the system.

Estimated flow rates during carbonation tests

A series of carbonation tests was run to monitor the output from the V-cone meter as well as the pressure-drop data across the mixing elements. The mixers and the V-Cone flow tube were removed and cleaned after each run in an attempt to ensure consistent system conditions. The performance of the flow tube during HTHP mineral carbonation runs was inferior to its performance during non-HTHP calibration runs. As the slurry reached higher temperature and pressure, the meter was prone to plugging. This was evidenced by excursions in the output data, (figure 4) with sometimes zero readings, sometimes wildly high readings that often returned to reasonable readings a short time later. The primary point of plugging was in the narrow channel inside the cone.

A more consistent way to measure flow may be by monitoring pressure drop across the static mixers; the pressure drop across the top mixer leg of the reactor was also recorded during the test series (figure 5). Although they experience a much larger pressure drop than the V-cone flow tube, the flow rate should also be proportional to the square root of this pressure drop. A k value was estimated during calibration or during carbonation during the periods when the V-cone was performing well. The mixers showed slightly more stable pressure drops than the V-cone tube, but the precision is also affected by the accumulation of solids in the mixer elements. The primary source of plugging solids appears to be pieces of scale that break off from interior surfaces of the pipes during a run. Analysis of the scale revealed that it is primarily unreacted mineral. Since conditions change from test to test, the amount of fouling is not constant.
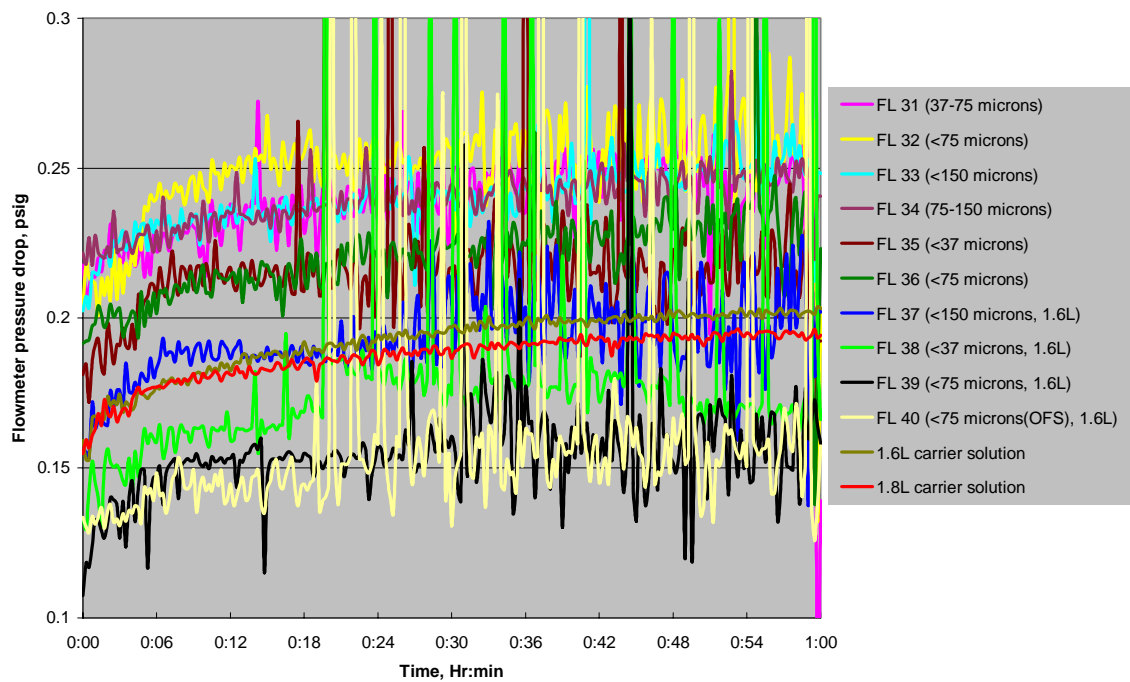
Figure 4 - Pressure drop across flowmeter during 1 hour reaction (pump speed 1450 rpm).
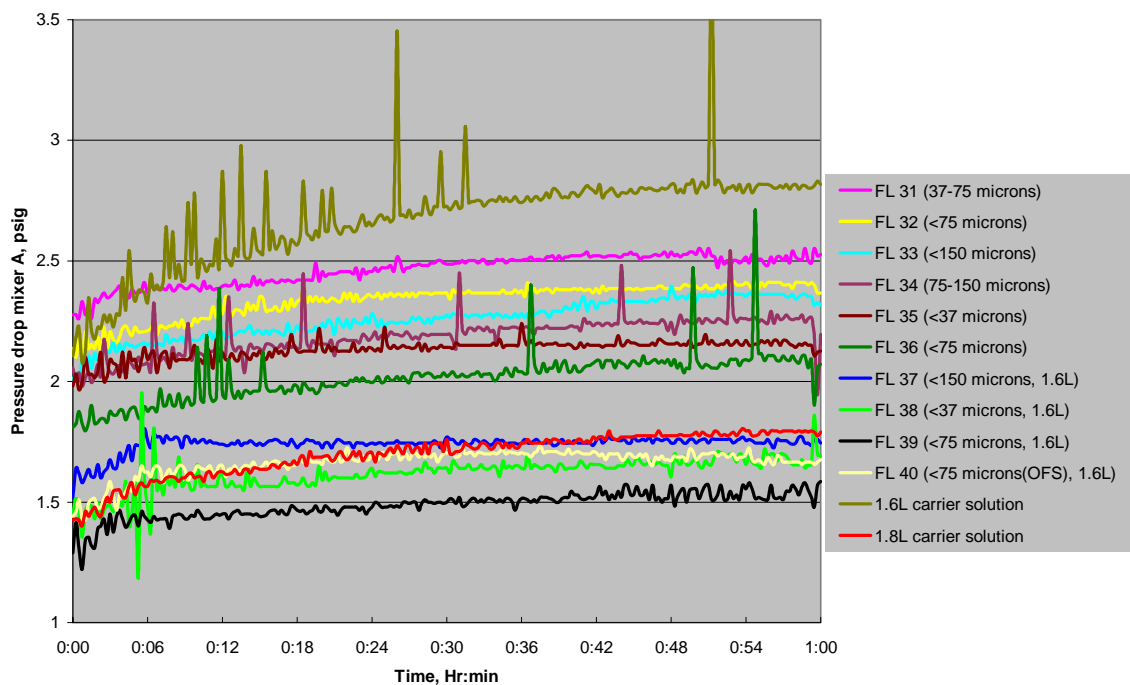
Figure 5 - Pressure drop across top mixer leg during 1 hour reaction (pump speed 1450 rpm).

If we assume that the ambient-condition calibrations are a good proxy for HTHP flow rates and use the k values 5.5 and 5.8 for the two fill volumes, the following flow ranges are obtained for the tests shown in figure 4: for 1.6L fill, the pressure-drop range of 0.16 to 0.21 psig yields a flow range of 2.2 to 2.5 gpm, and for 1.8L fill, the pressure-drop range of 0.21 to 0.26 psig yields a flow range of 2.65 to 2.95 gpm. More modeling is needed to determine whether ambient flow rate is a good proxy for HTHP flow rates. Although the pressure-drop methods are imprecise, the range is narrow enough to estimate energy requirements for long pipe lengths for the reactor.

Effects of particle-size distribution on carbonation reactivity

The other important challenge for improving the prospects for commercial application of mineral carbonation is to increase the reaction rates. Grinding the mineral feed finer is a proven way to speed up the reaction, but the grinding energy costs are prohibitive. Some of our previous work has suggested that some mineral samples may react faster in the HTHP flow-loop reactor than they do in a conventional autoclave. The flow through the pump, pipe, and static mixers may improve the carbonation reaction rate by increasing reaction flow turbulence, which should increase particle-particle and particle-wall collisions, and enhance passivating-layer exfoliation.

Preliminary modeling of slurry streams suggests that variation of the particle-size distribution may also be used to increase the collisions between particles and thus increase reactivity. To investigate these effects, a number of tests were performed using different size fractions of the same ore. The goal of the ore preparation was to obtain a wide distribution of particle sizes in the range of 0 to 150 micron particle diameters.

A Twin Sisters olivine ore was ground for 1 hour in a rod mill. The ground ore product was then wet-sieved into several size bands: the finest size passing a 400-mesh sieve (<37 microns), the middle size passing a 200-mesh sieve but not a 400-mesh sieve, (37x75 microns), and the largest particle size fraction passing a 100 mesh sieve but not a 200-mesh sieve (75x150 microns). Each fraction was analyzed for the primary reactive component, Mg, and found to be very homogeneous, approximately 30% Mg. The weight fraction found in each size range from smallest particles to largest was 46.2%, 25.5%, and 28.2%. Some of the fractions were analyzed for size distribution by sedimentation/x-ray absorption technique and others were estimated. The mean particle sizes (D_{50}) are shown in table 1.

Each size fraction was used as the feed in separate mineral carbonation tests. In other tests, they were combined to determine how the various combinations interact with respect to carbonation reactivity. Tests were generally run using 15% solids by weight in carrier solution that contained $0.64M$ $NaHCO_3$ and $1M$ $NaCl$. The slurry was injected into the reactor, pumped at 1450 rpm, and preheated to 185º C under a 150-psig atmosphere of CO_2, and then CO_2 was injected into the flow-loop reactor to reach a steady-state pressure of 2375 psig for the duration of the carbonation run. With the exception of test #30 (20 min), all the tests were run at pressure for 1 hour before the reaction was quenched with cooling water. The reaction product slurry was filtered, the solids were dried and analyzed for CO_2, and extent of reaction was calculated for each test. Results are tabulated in table 1.

Several of the tests were run with a 1.8L slurry fill, and others were run using 1.6L slurry fill. The lower fill allows a larger fraction of CO_2 bubbles to flow with the slurry during the test, and allows more interphase contact during flow. It also creates more cavitation in the pump and thus lowers flow rates.

Results of carbonation tests

The two coarsest mineral fractions by themselves were mostly unreactive – less than 2.5% extent of reaction (tests 31, 34, and 36). The amount of reactor fill (1.8L or 1.6L) made no significant difference. The finest fraction was reactive, resulting in reaction extents ranging from 34% to 40% (tests 35, 38, and 42). The combined smaller (< 75 micron) fractions (tests 32 and 39) were slightly less reactive (28% to 32%). Each of these results appears consistent with the others. When the bulk sample was tested, however (tests 33, 37, and 41), the reaction was limited to less than 2.5% extent of reaction, no significant improvement over samples comprised entirely of coarser fractions.

All of the reactive samples contained significant (>46%) quantities of fine particles, whereas widely size-dispersed feedstocks fell to insignificant reactivity when significant (>28%) quantities of coarse particles were included. Despite the substantial amount of fine-particle content, the presence of coarse particles seemed to have the unexpected result of quenching the reactivity of the mixture.

Three tests were run using the same ore, but ground two hours instead of one. The bulk sample passed a 200-mesh sieve (<75 microns) and had a D_{50} of 21 microns, as compared to an estimated D_{50} of 30 microns for the feed used for tests 32 and 39. These tests are highlighted in the table 1 (tests 28, 29, and 40). Reactivity was above 34% in all three tests, topping out at 43% on test 29. Both tests 28 and 29 were conducted with the spiral mixers shown in figure 3. Estimated flow rate was 3.1 gpm for test 28, which was run at a lower pump speed of 1198 rpm. No flow estimate is available for test 29, run at a higher pump speed 1452 rpm, but also with 30% solids.

Test	Feed size, microns	Particle size, D_{50}	Slurry volume, L	CO_2 analysis, %	Extent of carbonation, %
28	<75	21	1.8	15.9	34.3
29*	<75	21	1.8	19.1	42.9
30	<37	14	1.8	12.6	26.0
31	37x75	Est 56	1.8	0.59	1.04
32	<75	Est 30	1.8	15.3	32.3
33	<150 (head)	40	1.8	1.32	2.40
34	75x150	Est 110	1.8	0.77	1.40
35	<37	14	1.8	16.1	34.6
36	37x75	Est 56	1.8	0.47	0.83
37	<150 (head)	40	1.6	0.75	1.33
38	<37	14	1.6	18.2	40.2
39	<75	Est 30	1.6	13.4	27.7
40	<75	21	1.6	16.0	34.6
41	<150 (head)	40	1.6	0.96	1.70
42	<37	14	1.6	16.4	35.4
43	attrited	4	1.6	28.8	79.5
44	1:1 (75x150+ attrited)	Est 60	1.6	22.1	53.0

*This test used 30 wt% solids in the slurry – all others 15 wt%.

All carbonation times were 60 min, except test 30 (20 min).

Table 1 - Summary of carbonation test data.

Because of the surprisingly low rate of reactivity of the bulk sample, another test pair was proposed to further examine the effect of mixed sizes. A new sample was prepared using an

attritor to grind the ore further to a D_{50} of 4 microns. We had previously shown this material to be quite reactive, and test 43 showed a typical result of 79.5% extent of reaction. An equal mixture of the attrited material and the coarse fraction should react about 40%, if neither fraction has a strong effect on the other. The result in test 44 was surprisingly high at 53% extent of reaction, considering how strongly the coarse fraction had quenched the <37 micron fraction in other tests.

Several of these tests are plotted in figure 6 as a function of mean particle diameter (D_{50}). The unexpected variability in reactivity between the yellow data points at 40 microns (low reactivity) and the red data point at 60 microns (high reactivity) is not yet explained. The higher reactivity is seen for a sample that had no middle size band, just an extremely fine one and a coarse one. The low reactivity samples had a full distribution of sizes from fine to coarse. More work is needed to explain the mechanism for this difference and to form a strategy to exploit it for maximum reactivity.

Feed distributions are described as containing significant quantities of
1) particles between 75 micron and 150 micron (coarse), **2)** particles
that have been attrited, **3)** particles that contain neither of the first two,
or **4)** particles that contain both of the first two.
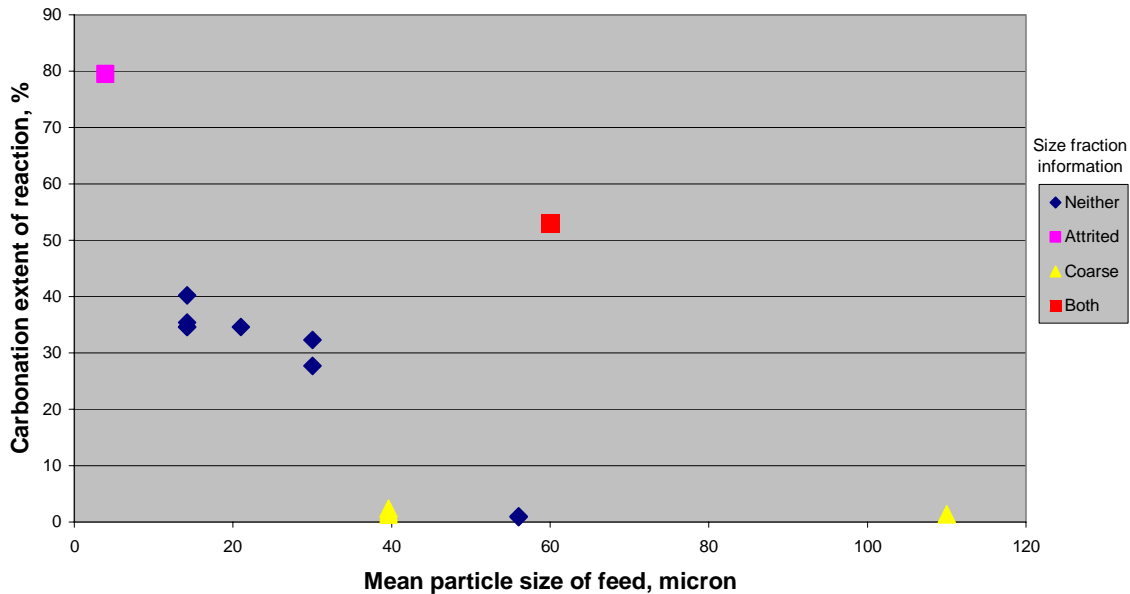
Figure 6 - Effect of mean particle size on extent of carbonation.

Conclusion

Progress was made on two challenges to improved continuous processing of CO_2 for stable sequestration: improved flow measurement and improved carbonation reactivity. A more reliable estimate was obtained for the flow rate of the multiphase fluid flow in the flow-loop reactor using pressure-drop metering. Progress continues in modeling the multiphase flow at HTHP conditions, coupled with ambient calibrations to estimate flow for a range of test conditions.

Experimental results show a disparity between the reactivity of chemically similar feedstocks. Ground ores that contain a significant coarse fraction, 75x150 microns, suffer poor reactivity unless a significant portion of the ore is attrited to ultrafine sizes (less than

4 microns). Additional tests and modeling studies are planned to determine the mechanism for this difference and to form a strategy to exploit it for maximum reactivity.

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