Laboratory Tests of Mafic, Ultra-Mafic, and Sedimentary Rock Types for In-Situ Applications for Carbon Dioxide Sequestration

G.E. Rush, W.K. O'Connor, D.C. Dahlin, L.R. Penner, S.J. Gerdemann
Albany Research Center, Office of Fossil Energy, US DOE

ABSTRACT

Recent tests conducted at the Albany Research Center have addressed the possibility of in-situ storage of carbon dioxide in geological formations, particularly in deep brackish to saline non-potable aquifers, and the formation of secondary carbonate minerals over time within these aquifers. Various rock types including Columbia River Basalt Group (CRBG) drill core samples, blocks of ultra-mafic rock and sandstone were used. A solution formulated from aquifer data, a bicarbonate-salt solution, and distilled water were tested. Pressure and temperature regimens were used to mimic existing in-situ conditions, higher temperatures were used to simulate longer time frames, and higher pressures were used to simulate enhanced oil recovery (EOR) pressure. Results are encouraging, indicating mineral dissolution with an increase of desirable ions (Ca, Fe^{2+}, Mg) in solution that can form the carbonate minerals, calcite ($CaCO_3$), siderite ($FeCO_3$), and magnesite ($MgCO_3$).

INTRODUCTION

The Department of Energy's Albany Research Center, (ARC), Albany, Oregon, has conducted laboratory tests of carbon dioxide (CO_2) sequestration through mineralization for the past 5 years. Over 600 batch autoclave tests have yielded a wealth of information on the effects of time, temperature, pressure, solution chemistry, and mineral reactivity, as well as data from grinding and energy studies to help determine the practicality of such a process. This research focused on development of an ex-situ process dealing with anthropogenic CO_2, created mostly from the burning of fossil fuels for power generation. Silicate rocks high in CaO, FeO, and MgO, (wollastonite, olivine, and serpentine, in particular), as well as less likely though more abundant mafic candidates such as basalt, gabbro, and sedimentary sandstone, have been evaluated.

Although results of up to 80% conversion of the silicate rock to carbonate in as little as 30 minutes in autoclave tests look encouraging, mining, mineral preparation, and reactor costs, as well as currently unresolved environmental issues, look to be prohibitive (O'Connor, *et al*. 2004). This conclusion led to the investigation of in-situ (underground) carbonation as a potential method of CO_2 sequestration.

The injection of CO_2 into geological formations is certainly not new. The practice has been used for years in EOR and coal-bed methane recovery. This current research looks at the potential for mineral sequestration of CO_2 by formation of reasonably stable secondary carbonate minerals within deep brackish to saline aquifers. It is theorized that a carbonate curtain will form, helping to seal the CO_2 in mineral and supercritical fluid forms. In formations with favorable mafic or ultra-mafic mineralogy, a significant portion of the injected CO_2 may be mineralized.

HISTORY

Proof-of-concept tests for in-situ carbonation took place in a stirred batch autoclave reactor at 185°C and P_{CO2} of 150 atm for 6 hours in an aqueous solution of 0.64M $NaHCO_3$, 1M NaCl. The pressure, temperature, and solution are the standard conditions used in the ex-situ work for baseline evaluation of reactants. The 6-hour, rather than standard 1 hour test time, was chosen to ensure enough time was allowed for reaction to take place with the chosen minerals.

In a typical test, 15% slurry of mineral and solution was loaded into the autoclave which was purged with CO_2, and the pressure was held at 150 psi (10 atm). The solution was stirred and heated for 1 hour to reach a temperature of 185°C, and then pressurized to 2375 psi with CO_2, (2250 psi partial pressure CO_2) and the test was started. At the end of the test, the system was cooled below 85°C, the pressure was bled off, and the slurry was collected. The solids were then separated from

1

the solution in a pressure filter, dried and sampled. Both solids and solution were analyzed.   Tests on basalt and its primary minerals, augite, anorthite, and olivine were run to determine carbonation potential. Additional tests on fayalite (Fe_2SiO_4) were run to verify that siderite ($FeCO_3$) would form and labradorite, a feldspar common to mafic rock, was also run. All the samples were attrition-ground to ensure ultra-fine particle size (minus 400 mesh). Many tests on olivine resulted in better than 80% conversion to carbonate, and all the other samples showed carbonation potential, from a high of 39% conversion for augite to a low of 11% for labradorite.
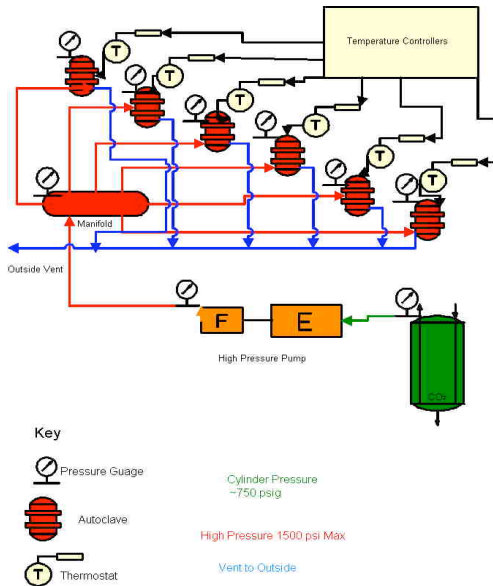
Materials and Methods

Figure 1. Schematic of autoclave reactor layout for pressure leach tests.

The equipment for the in-situ work included a manifolded series of six two-liter autoclaves capable of maintaining pressure of 1900 psi and temperatures of 100˚C (Figure 1). A pneumatic high-pressure pump was used to maintain 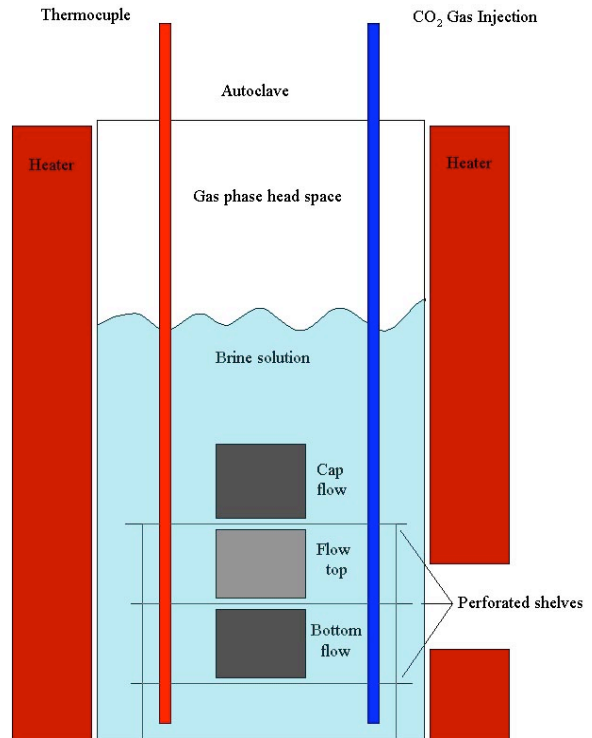the various test pressures. Up to three samples were placed into each autoclave and sat upon perforated stainless steel shelves to ensure complete contact and immersion in the 1.5 liters of brine or carbonation solution in each autoclave. Temperature was held constant by thermostat-controlled electric element heaters that surround each autoclave, while CO_2 was supplied to each autoclave from a high-pressure manifold. A cross-section of the autoclave reactor is included as Figure 2.

Figure 2. Core emplacement in autoclave.

Two series of autoclave tests under in-situ simulated conditions have been completed in the last year (2003). Test series 1 used two sets of drill core samples of CRBG from depths between 3000 and 4000 feet. One set was from the porous inter-flow zone, with porosity from 17 to 40%, and a second set was from a massive section with porosity of zero to 5%. (Appendix 1) The massive sections of the CRBG act as aquitards or aquifuges, isolating the aquifer within the inter-flow sections. The fact that a mafic sequence like the CRBG hosts extensive aquifers (Whitehead 1994) could make it an ideal candidate for geological sequestration, with potential for both hydrodynamic and mineral trapping of injected CO_2 (O'Connor, *et al*, 2003). These characteristics make it an excellent choice for the first series of tests. Samples were approximately 1.5-inch diameter and 1 inch thick (Figure 3). Weights, densities, and porosities were determined before and after the tests. Bulk chemical analysis and X-ray diffraction analysis (XRD) of the solids were also acquired. In an effort to simulate actual conditions within the formation, test solution chemistry and temperature (35˚C) were taken from known aquifer data (Reidel *et al*. 2002). Half the samples were run at 300 psi, the estimated water column pressure at aquifer depth, and the other half at 1500 psi, a typical EOR injection pressure. CO_2 was sparged through the autoclaves twice daily to simulate injection flow. In the first basalt series, Is 1-10 and Is 15-16, the first eight tests were run for a specific time; solution and solids were then analyzed.

Figure 3. Sectioned core from CRBG T: top, cap rock; M: middle, flow top zone; B: bottom

In test Is 9-10, and 15-16, solution samples were taken during the runs at 100, 500, 1000, and 2000 hours to track solution changes, and the solids analyzed only at the conclusion of the tests.

The rocks used in test series 2 included Twin Sisters olivine from northwest Washington; two serpentines, antigorite from southeastern Pennsylvania, and lizardite from southwest Oregon; and Tyee sandstone from western Oregon. The olivine and serpentines were chosen because much is known of their carbonation potential from previous ex-situ work, and their abundance. Both rocks tend to form massive jointed formations containing few or no aquifers, so their practicality as in-situ carbonation sites needs to be evaluated. Two additional core samples of CRBG were used in a higher temperature test (90˚C) in the second round of tests.

The standard bicarbonate-salt solution (0.64M $NaHCO_3$, 1M NaCl) was used for the second series of tests. Samples other than the basalt were rough 1-inch cubes. Test conditions for the second series of tests on the serpentines, olivine, and sandstone were 60˚C and 1500 psi, and 90˚C and 1500 psi for the basalt. Solution samples were analyzed at the start of the tests and at 100, 500, 1000, and 2000 hours during the second series of tests. The second series of tests was conducted in the same method as tests Is-9 and Is-10. Solution samples taken at specific times, . and solids were sampled only at the conclusion of the test. Temperature and pressure are monitored and recorded for each autoclave.

Sample	MgO	CaO	FeO	Total Oxides	SiO$_2$
Antigorite	40.62	0.28	2.07	42.97	37.65
Lizardite	37.31	0.66	3.8	41.77	38.29
Olivine	49.74	0.65	8.1	58.49	40.01
Basalt Porous	2.61	17.06	7.05	26.72	54.7
Massive	3.44	17.56	11.27	32.27	51.77
Gabbro	7.76	17.88	15.18	40.82	43.23
Tyee Sandstone	1.76	7.4	3.82	12.98	63.75

Table 1. Comparison of starting materials oxides, wt pct

Table 1 shows percentage of major oxides available to form the secondary carbonate minerals, magnesite ($MgCO_3$), siderite ($FeCO_3$), calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$), and ankerite ($CaCO_3(Mg, Fe)CO_3$) and silica percent. Table 2 shows test conditions for all tests including reactant, temperature, pressure, solution chemistry, pH, and time.

Table 2, test conditions

Reactant	Is test #	Temp. ˚C	Pressure psi.	Solution	Time, hrs.	Start, pH	End, pH
CRBG	1	35	300	Simulated aquifer	100	9.24	5.94
CRBG	2	35	300	Simulated aquifer	500	9.24	5.78
CRBG	3	35	300	Simulated aquifer	1000	9.24	5.74
CRBG	4	35	300	Simulated aquifer	2000	9.24	6.05
CRBG	5	35	1500	Simulated aquifer	500	9.26	6.34
CRBG	6	35	1500	Simulated aquifer	100	9.26	5.45
CRBG	7	35	1500	Simulated aquifer	1000	9.26	5.69
CRBG	8	35	1500	Simulated aquifer	2000	9.26	5.77
CRBG	9	35	300	Simulated aquifer	2000	9.26	5.66
CRBG	10	35	1500	Simulated aquifer	2000	9.28	5.60
Olivine	11	60	1500	Carb. solution	100, aborted	7.58	7.63
Antigorite	12	60	1500	Carb. solution	2000	7.58	7.55
Lizardite	13	60	1500	Carb. solution	1000	7.58	7.58
Sandstone	14	60	1500	Carb. solution	2000	7.58	7.51
CRBG	15	90	1500	Carb. solution	1000	7.58	7.61
CRBG	16	90	1500	Simulated aquifer	2000	9.10	8.01
Olivine	17	90	1500	Distilled water	2000	6.21	8.36
Olivine	18	60	1500	Carb. solution	2000	7.85	7.98
Gabbro	19	90	1500	Distilled water	2000	6.21	8.13

CRBG=Columbia River Basalt drill core. **Olivine**=Twin Sisters Olivine. **Antigorite**=antigorite serpentine. **Lizardite**=lizordite serpentine. **Sandstone**=Tyee sandstone. **Gabbro**= Duluth gabbro. **Pressure, psi**=total pressure, (p_{CO2}+water vapor pressure). **Simulated aquifer**= 97 mg/L $NaHCO_3$ 30 mg/L Na_2CO_3, 207 mg/L Na_2SO, 410 mg/L NaCl, 110 mg/L NaF, 11.2 mg/L KCl. **Carb. solution**= .64M $NaHCO_3$, 1M NaCl**. Start pH** =pH of starting solution. **End pH**=pH at end of test. Some tests had solution samples taken during the test, and intermediate pH is not shown here.

DISCUSSION

Test Series 1: Basalt Core Tests

Figure 4 shows the change in solution concentration over time for Ca, Fe, Mg, and Si, at 35˚C and 300 psi. The analysis of the starting solution is shown at 0 hours. Each test used a different core sample and a different test time. This was done so solid and solution analyses for given times could be compared.
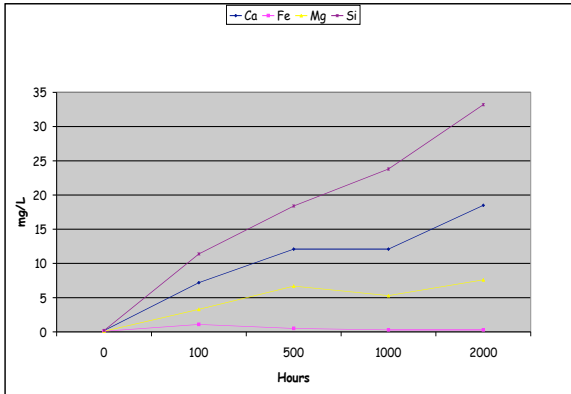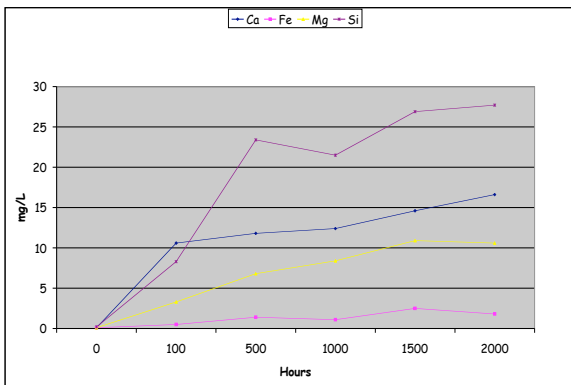

When the test results are plotted together against time they show a steady increase of cations in solution, indicating dissolution of solids. This dissolution primarily involves existing secondary minerals in the porous interflow core, but all cores showed increased porosity and weight loss during the tests.

Figure 5 shows solution concentrations over time for Ca, Fe, Mg, and Si, at 35˚C and 1500 psi. Again a steady increase of cations and silica in solution are shown indicating dissolution of solids. The slightly higher concentration values of a given time compared to figure 6 indicates that the higher CO_2 pressure (1500. versus 300 psi) results in more aggressive dissolution. Increased porosity and weight loss were noted in all the tests (Appendix 1).

Figure 4. Is 1-4 solution analysis trends.

Tests Is-9 and Is-10 differed from tests Is 1-8 in that solution samples were taken at time intermediate times during each test to look at the evolution of the solution. The solids were analyzed only at the end of the tests.

Is-9 used the same test conditions as Is 1-4 (35˚C and 300 psi), and figure 6 (Is-9) shows a general increase of cations in solution, quite similar to that in figure 4 (Is 1-4). The Fe and Mg concentrations peak around 1500 hours and then level off. This may indicate the saturation level for Fe and Mg at this temperature and pressure in this solution.

Is-10 used the same conditions as Is 5-8 (35˚C and 1500 psi). Figure 7 (Is-10) shows the increase of desirable cations and leveling off of Fe and Mg around 1500 hours. Very little difference is seen between tests Is-9 and Is-10.

Figure 5. Is 5-8 solution analysis trends.

The pH of the solutions is interesting (Figure 8) and may explain the observed results. The starting solution has a pH above 9, and then drops quickly to around 5.5 due to the CO_2 injected into the solution at temperature. The desired carbonates may not form at this low pH. The solutions reverted to the approximate starting pH of 9 some months after the tests were completed and the CO_2 had left the solution, quite like a beer going flat over time. In some of the porous basalt core samples, siderite ($FeCO_3$) was identified. This formed naturally in the brackish alkaline aquifers during the 15 million years or so since the basalts were emplaced

Figure 6. Is-9 solution analysis trends.

Figure 9 shows Is-16 solution trends at 90°C and can be compared with figure 6 (Is-10), which used the same test conditions except that the temperature was 35°C. Is-16 did not spurge CO_2. CO_2 was injected only to maintain test pressure.
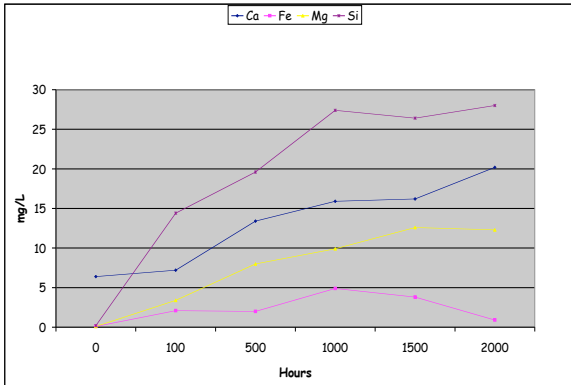
The higher temperature tripled the Mg concentration, halved the Fe. and Si concentrations and the Ca concentration was similar for both tests. The higher temperature in this case appears to hold to the adage that the higher the heat, the quicker the reaction. This is not the total story. The solution pH is a primary factor and explains the observed results. The previous basalt tests, Is 1-10, that was twice daily sparged with CO_2 lowered the pH to ~5.5. (Figure 8). The pH of Is-16 stayed around 7.5 and is friendlier for Mg liberation. The solution chemistry indicates much higher concentration of CO_2 at the higher pH (Is-16). At pH 7.5 the majority of the CO_2 is a buffered HCO_3^- species, not the more acidic aqueous H_2CO_3 species at pH 5.5.
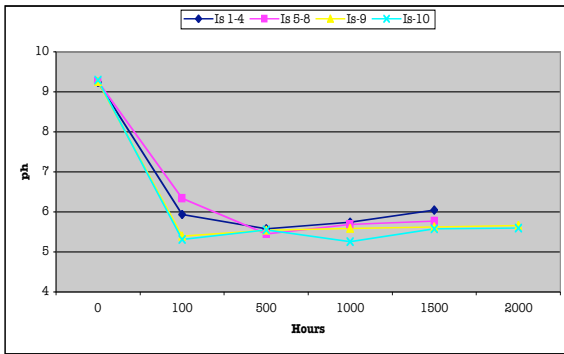
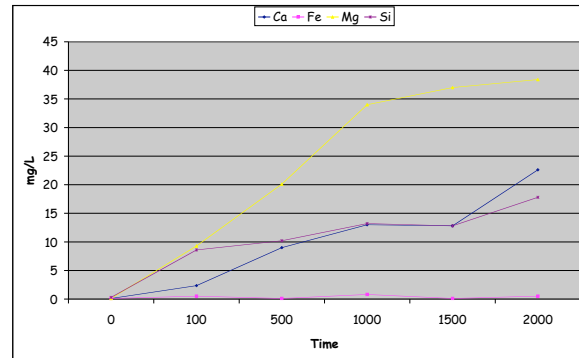**Figure 7. Is-10 solution analysis trends**

Figure 8. Is1-10 solution pH

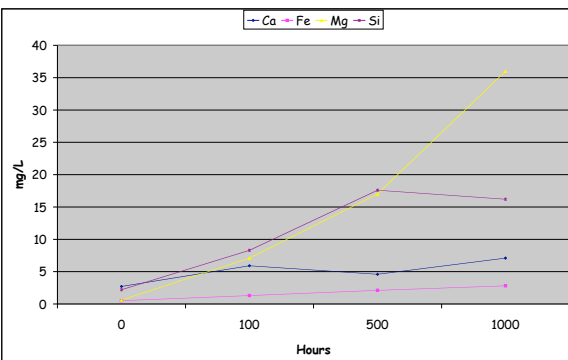**Figure 9. Is-16 (CRB, 90°C, 1500 psi) solution analysis trends.**

This can be explained by the solubility of CO_2 as a function of temperature and pressure. At constant pressure, temperature has a direct effect on aqueous CO_2 solubility: as the temperature increases, the solubility of aqueous CO_2 decreases. Less aqueous CO_2 in solution causes the pH to rise by forming bicarbonate (HCO_3^-) and favors Mg over Si dissolution.

Is-15 (Figure 10) used the same conditions as Is-16 but the latter used bicarbonate-salt solution (0.64M $NaHCO_3$ 1M NaCl); Is-15 used the simulated aquifer solution. Both solution analyses are similar. Again the higher pH is more selective for Mg, while the lower pH is more selective for Si (Figures 4-7). Ca concentrations in the basalt are lower than expected, because the basalt contain 3 times as much Ca as Mg (Table 1). Apparently anorthite ($CaAl_2Si_2O_8$), the primary Ca mineral in basalt, is slow to break down at test conditions.

Figure 10. Is-15 (CRB, 90°C, 1500 psi) solution analysis trends.

Fig. 11 shows the pH trends for Is 12-16. Is-16 used the aquifer solution with a starting pH of 9.2, which quickly moved to about 7.3. The others used the bicarbonate-salt carbonation solution with an initial pH of 7.6 that basically stayed in this range. The higher temperature (90°C) at 1500 psi favors HCO_3^- over H_2CO_3 in solution. XRD and bulk chemistry of the after-test samples gave no indication of the formation of secondary carbonate minerals. Possibly the cation concentrations never reached the threshold of precipitation or the temperature and pressure regimes are prohibit the formation of carbonates,

and though some samples from the higher pH tests showed slight CO_2 increases in the bulk analysis and may form carbonate if given longer test times.
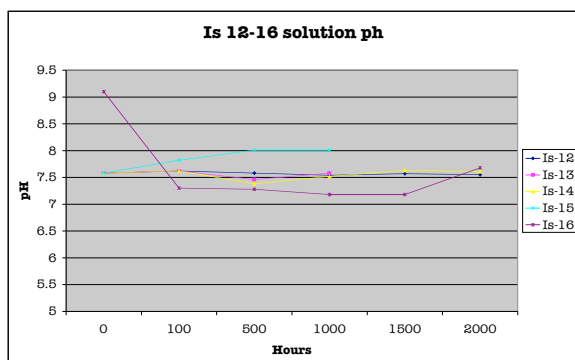

Figure 11. Is 12-16 pH trends

The tests on the cores show that basalt will give up cations to solution, setting up the possibility of the formation of secondary minerals. Pre-existing secondary minerals are dissolved initially from the porous basalt, which accounts for most of the rise in cation concentrations in solution. All of the massive samples in the test showed very little changes in weight and porosity. Much longer tests are needed to determine the fate of the glassy matrix of the basalt.

The excess solutions from the first ten tests were filtered when precipitates were noted in the archived samples. The volume of collected solids was not sufficient for bulk chemistry. XRD indicated a largely amorphous pattern. X-ray fluorescence (XRF) indicated Si, Al, Fe, and Ca as major components with trace elements such as Cr and Ni. The major elements noted are those that make up the bulk of basalt mineralogy and indicate that at least some of the basalt was put into solution.

Test Series 2: Ultra-mafic and Sandstone Block Tests

 The second series of tests was run on samples of olivine, serpentine (antigorite and lizardite) and sandstone. The tests (Is 11-14 & 18) were run at 60°C and1500 psi for 2000 hours, with solutions sampled at 100, 500, 1000, 1500, and 2000 hours. In addition to these tests, olivine and gabbro were run in distilled water at 90˚C and 1500 psi as baselines for comparison with other solutions.   They were sampled as above. The same analysis procedures were followed including weight, density, porosity, and chemistry, before and after each test.   In this series, CO_2 was not sparged daily, but only added to maintain the test pressures. The 0.64 M NaCl, 1 M $NaHCO_3$ bicarbonate-salt solution was used for tests Is-11through Is-14. The bicarbonate solution was used to allow comparison of results with those of the proof-of-concept batch tests using the stirred autoclave reactor.

 Is-16 used the simulated aquifer solution to look at the effects of higher temperature, and results were compared to the high-pressure basalt test (Is 5-8 &10). Table 2 shows reactants and conditions for the tests in series 2. Is-11 was aborted after a serious leak and check valve problem, so results are unavailable. Is-12 used antigorite serpentine, and the solution chemistry is shown in Figure 12. The Mg concentration peaks at 1000 hours and then levels off, indicating the saturation level for Mg at temperature and pressure. Bulk chemistry of the post-test solids found CO_2, and XRD identified magnesite ($MgCO_3$) in the solids. The Ca, Fe, and Si are near expected levels ~10 mg/L, antigorite typically has less than 5% Ca, and Fe in the rock.

 The low Si concentration mirrors results from the stirred autoclave tests, which showed approximately 10 times more Mg than Si in solution. The pH of the buffered solution stayed around 7.5 throughout the test, which appears to be more selective for Mg dissolution. The more acidic solution attacks Si, as in the first series of tests, where the pH stayed around 5.5 throughout the tests.
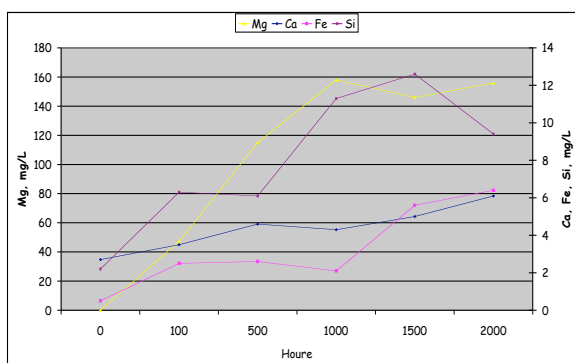

Is-13 used lizardite serpentine and has a very similar solution graph (Figure 13) when compared to Figure 12. Again the bicarbonate solution was selective for Mg, as indicated by the similar dissolution concentrations in the 2 tests. The bulk chemistry and XRD again confirmed CO_2 in the post-test solids in the form of magnesite. The lower concentration for Mg at 1000 hours in the lizardite test as compared to the antigorite test is consistent with the stirred autoclave tests. The reason for this is beyond the scope of this paper, but likely has to do with differences in crystal structure between the two minerals and the possible presence of more soluble brucite, $Mg(OH)_2$ in the antigorite. The test ended prematurely due to a faulty check valve.
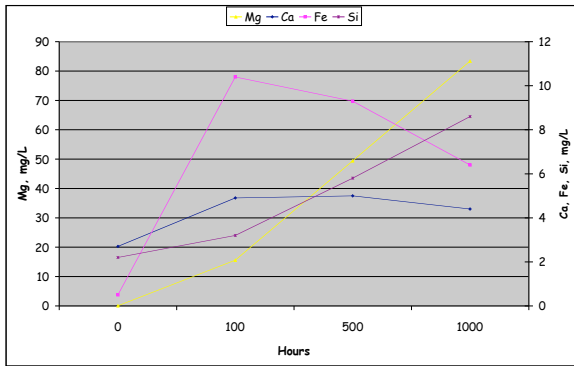
Figure 12. Is-12 (antigorite, 60˚C, 1500 psi, carb. solution) analysis trends

Figure13. Is-13 (lizardite, 60˚C, 1500 psi, carb. solution) analysis trends.
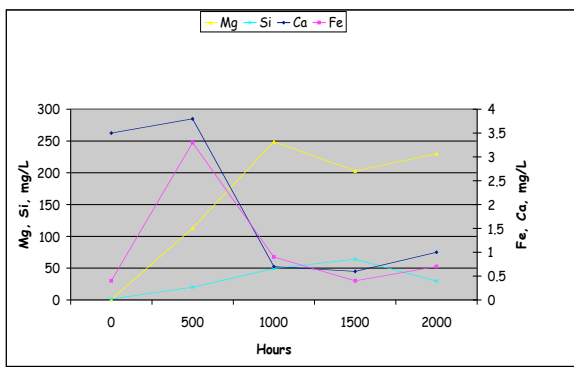

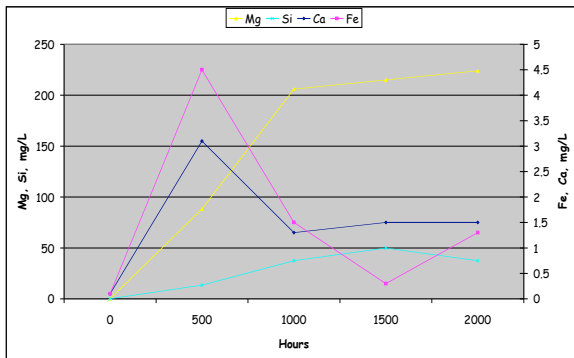**Figure 14. Is-18 (olivine, 60˚C, 1500 psi, carb. solution) analysis trends.**

Figure 15. Is-17 (olivine, 90˚C, 1500 psi, water) solution analysis trends.

Is-14 (Figure 17) used Tyee sandstone from western Oregon. As is typical in sandstones, SiO_2 makes up the majority of the rock, ~62% by weight The Tyee is a dirty sandstone with significant amounts of other oxides (MgO~2%, CaO~8%, and FeO~4%) that can add to the cation concentration in solution. The solution chemistry shows that some of the desired cations were liberated from the rock, although no carbonate minerals were identified by XRD. Bulk chemistry of the post-test solids indicated a slight increase in. CO_2 (0.8%, up from an initial 0.7%).

Is-18 (Figure 14) was a rerun of the aborted Is-11. The Mg concentration rose and leveled off at 1000 hours, at which time Fe, Ca, and Si almost stabilized. The high Mg concentration is expected with the favorable conditions of this test. XRD found no carbonate, although the bulk chemistry indicated a slight CO_2 content in the solids.

Is-17 (Figure 15) used olivine at 90˚C in distilled water. The solution begins to stabilize at 1000 hours with the Mg continuing to slowly climb rather than leveling off, indicating that saturation was not reached at this T&P in water. XRD revealed no carbonates in the after-test solids, but bulk chemistry showed a small amount of CO_2.

The higher temperatures used for Is-12, 13, & 18 (60˚C) and Is-17 (90˚C), as well as the bicarbonate solution used in Is-12, 13, &18 affect the solution pH by changing CO_2 solubility for a given pressure, as shown in Figure 16. In all four cases the Mg concentration increased while the Si concentrations remained low.

Both the distilled water and bicarbonate solution stabilized between pH 8 and pH 8.5 with injection of CO_2, again showing the buffering effect of the HCO_3^-/H_2CO_3 ratio in the solution.
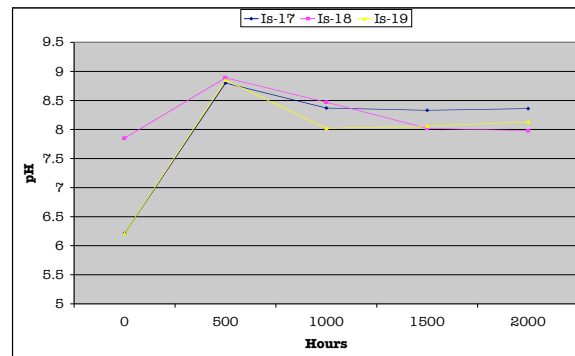
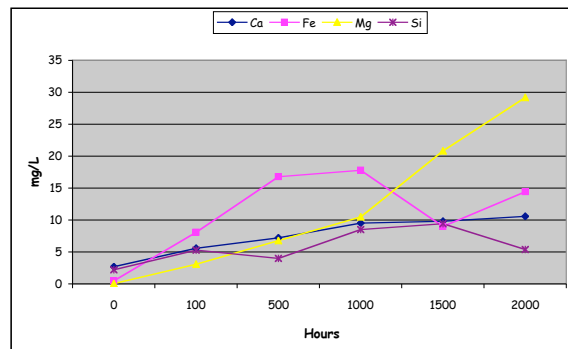

Figure 16, Is 17-19 solution pH analysis trends

Figure 17. Is-14 (sandstone, 60˚C, 1500 psi) solution analysis trends.
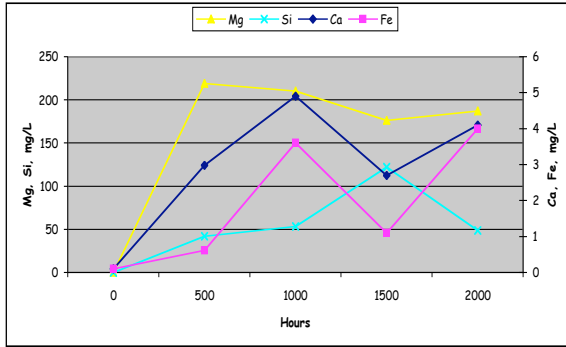
Figure 18. Is-19 (gabbro, 90˚C, 1500 psi, water) solution analysis trends

The final test in the series used gabbro, an intrusive rock chemically similar to basalt, but having generally larger mineral grains. Gabbro is common in the lower sections of mafic and ultra-mafic formations. A gabbro gravel (1500 g) was used in the hope of reaching saturation levels for the desirable cations, followed by precipitation of carbonate minerals.

Figure 18 shows a quick jump in Mg concentration, a much higher Mg dissolution rate despite the much lower concentration of Mg in the gabbro compared to the olivine (4.6 and 31% respectively). The higher dissolution rate is likely due to finer particle size (1/2" x 3/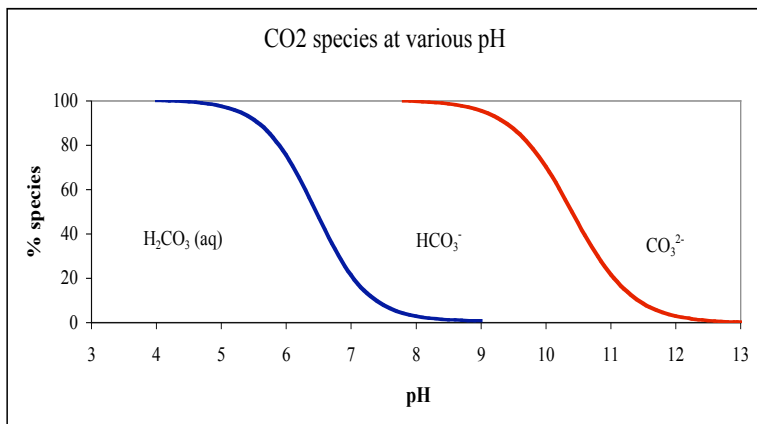4" gravel versus 1" blocks) and greater mass (1500g versus ~70g) that resulted in greater surface area of the gabbro sample versus the two olivine samples. Tests Is-17 and Is-19 were both conducted in distilled water, and perhaps more significant than the rate of Mg dissolution is the Mg concentration, which appears to level off at just over 200 mg/L for the gabbro (Is-19). This may mark the maximum solubility for Mg at this pressure, temperature, and pH; the Mg concentration for the olivine test (Is-17) also levels off at about 200 mg/L. XRD identified no carbonates, although bulk chemistry of the after-test solids found a slight increase of CO_2 (0.23% to 0.46%).

Figure 19. CO_2 species at pH. (from Hem 1989

Figure 19 shows CO_2 species for given solution pH and explains the pH variations observed among tests using CRBG, when temperature was the only difference in the test conditions. Is-10 and Is-16 illustrate this condition and its ramifications. Test Is-10 was conducted at 35˚C and 1500 psi with simulated aquifer solution. Is-16 was conducted under the same conditions except at a higher temperature of 90˚C. The Is-10 solution analysis (Figure 7) shows Si to be the dominate ion in solution and Mg is less than half that of Si. The Is-16 solution analysis (Figure 9) shows Mg levels 3 times higher, and the Si concentration is roughly half that of Is-10. The pH of Is-10 was ~5.5, while the pH for Is-16 was ~8. The elevated temperature lowered the aqueous CO_2 solubility, forcing CO_2 out of solution moving the pH up where bicarbonate (HCO_3^-) is favored over carbonic acid (H_2CO_3), as indicated in figure 19. With this shift the solution becomes a more aggressive solvent for Mg and less so for Si. Figure 20 shows Is-10 and Is-16 solution analyses graphed together and clearly shows the effect of the temperature change.

The information on pH, temperature, and pressure relationships discovered during these tests supports the theory for the formation of a carbonate curtain within the aquifer. At aquifer temperatures (35˚C), the introduction of CO_2 drives the pH of the solution down, making it acidic. This causes the dissolution of secondary minerals and the liberation of Si, as shown in the solution graphs for tests Is 1-10. This is a picture of conditions relatively close to the injection site. Down stream from the injection site, the CO_2 concentration in solution will decrease and allow the pH to possible rise to the point that carbonates will form from desirable cations in solution. Continued injection would theoretically continue to push this carbonate curtain away from the injection site. This brings up the question of when to stop injection of CO_2 into a given aquifer.
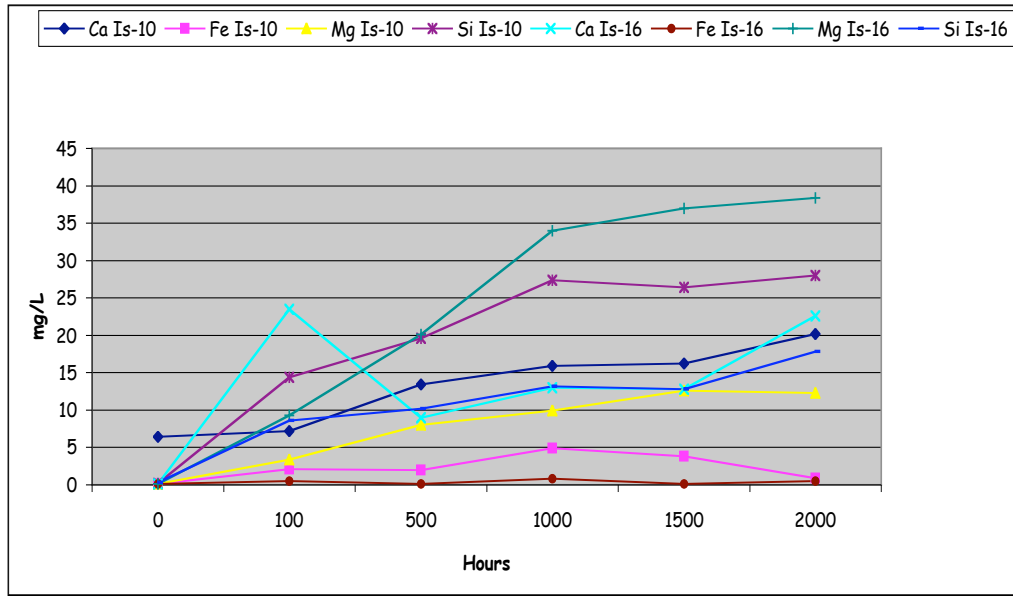
Figure 20. Is-10 and Is-16 solution analyses trends

Conclusions

The 18 tests conducted to date offered insight into aspects of in-situ sequestration of gaseous CO_2. All samples tested showed dissolution of secondary and/or primary minerals within the rocks. The release of Mg, Ca, and Fe^{2+} cations to the solution makes formation of secondary carbonate minerals possible. Chemical analysis of the after-test solids found slight increases of CO_2 in several samples, and XRD identified magnesite ($MgCO_3$) in the two serpentine tests. XRD and chemical analysis identified increases of CO_2 or the formation of magnesite only in the tests conducted at the higher temperatures (60 and 90˚C) and at pH of 7 or higher. Solution chemistry is clearly a function of temperature, and consequently tests of higher temperature do not effectively simulate longer time frames at in-situ conditions particularly for these high-P_{CO2} tests. The use of higher temperatures to expand the time-scale of the experiment requires the use of higher relative pressure to account for the lower aqueous CO_2 solubility and CO_2 species shift causing altered mineral dissolution at the elevated temperature. This methodology may more effectively simulate the injection of CO_2 into the aquifer at the in-situ temperature. Aquifer temperature, pH, solution chemistry, and mineralogy are all factors in the selection of target aquifers where mineral carbonation is desired.

References

Hem, J.D. USGS Survey Water-Supply Paper 2254 1989. "Study and Interpretation of the Chemistry of Natural Waters" 3rd Addition, pg. 107, Fig. 19

O'Connor, W.K., Dahlin, D.C., Nilsen, D.N., Gerdemann, S.J., Rush, G.E., Penner, L.R., Walters, R.P., and Turner, P.C. 2003. "Continuing Studies on Direct Aqueous Mineral Carbonation for CO_2 Sequestration." Proceedings, 27th International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, Florida.

O'Connor, W.K., Dahlin, D.C., Rush, G.E., Gerdemann, S.J., Penner, L.R., Nilsen, D.N. Jan. 30 2004. "Aqueous Mineral Carbonation: Mineral Availability, Pretreatment, Reaction, Parametrics, and Process Studies" DOE/ARC-TR-04-0002

Perry, R.H., Green, D. "Perry's Chemical Engineers' Handbook" 6th Addition pg. 3-101, Table 3-125

Reidel, S.P., Johnson, V.G., Spane, F.A. 2002. "Natural Gas Storage in Basalt Aquifers of the Columbia Basin, Pacific Northwest USA: A Guide to Site Characterization." PNNL-13962.

Whitehead, R.L. 1994b. "Columbia Plateau Regional Aquifer System." USGS Ground Water Atlas of the United States Idaho, Oregon, Washington. HA 730-H.

Appendix 1: Prior and after-test weight, density, and porosity of in-situ reactants.

Test Is # Sample ID	Pre-test Wt, grams	Pre-test density g/cc	Per-test porosity %	Post-test Wt. grams	Post-test density g/cc	Post-test porosity %
Is-1						
FT 4	59	2.58	25.3	55.7	2.88	29.2
UM 4	74.8	2.84	1.8	74.9	2.88	2.8
Is-2						
FT 3	56.6	2.63	27.5	54.3	3.33	
UM 3	79.7	2.85	1.9	79.7	2.86	2.1
Is-3						
T4	78.7	2.85	0.0	78.7	2.86	0.0
M4	46	2.67	38.1	43.5	2.79	43.5
B4	73.8	2.86	0.0	73.7	2.86	2.7
Is-4						
T5	77.8	2.85	0.0	77.8	2.88	0.0
M5	42.3	2.51	35.9	38.6	2.86	48.7
B5	70.8	2.85	0.6	70.1	2.88	2.7
Is-5						
T3	69.4	2.84	0.0	69.4	2.88	0.0
M3	42.9	2.64	38.6	40.2	2.88	47.1
B3	69.6	2.86	0.5	68.3	2.94	5.1
Is-6						
FT 1	59.2	2.63	17.4	56.9	2.79	25.2
UM 1	77.9	2.85	1.9	77.6	2.84	1.9
Is-7						
T2	78.6	2.83	0.0	78.6	2.9	0.0
M2	42.1	2.64	39.5	39.4	2.81	46.9
B2	69.1	2.84	2.6	68.2	2.87	5.1
Is-8						
T1	68.7	2.85	3.5	68.5	2.90	5.4
M1	46.6	2.69	35.8	45.1	2.85	41.4
B1	66.2	2.84	6.8	65.8	2.85	7.7
Is-9						
FT 2	53.0	2.60	28.9	50.9	2.76	35.7
UM 2	78.9	2.86	1.8	78.8	2.88	2.7
Is-10						
FT 5	54.4	2.67	25.3	52.9	2.74	29.2
UM 5	74.8	2.84	1.8	74.9	2.88	2.8
Is-11						
TSO 1	66.9	3.31	1.5	66.9	3.35	2.8
Is-12						
Antig 1	43.0	2.68	6.8	41.9	2.72	10.6
Is-13						
Liz 1	43.2	2.64	5.2	43.0	2.62	5.0
Is-14						
S3A	41.3	2.73	21.3	41.5	2.71	20.2
Is-15						
CRB I 1	54.0	2.72	21.3	54.4	2.82	23.5
CRBM 1	60.4	2.83	2.1	60.5	2.81	1.3
Is-16						
CRB I 2	43.9	2.8	32.4	42.5	2.96	38
CRBM 2	71.7	2.84	4.0	71.6	2.84	4.0
Is-17						
TSO 3	60.6	3.3	2.2	60.1	3.41	5.8
Is-18						
TSO 4	73.4	3.3	1.4	73.1	3.33	2.7
Is-19						
Gab 1	1500	2.97		1498	2.97	