

INTERACTION OF ROCK MINERALS WITH CARBON DIOXIDE AND BRINE: A HYDROTHERMAL INVESTIGATION

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INTRODUCTION

This paper presents interim results of a feasibility study on carbon dioxide (CO₂) sequestration in deep saline formations. The focus of the investigation is to examine factors that may affect chemical sequestration of CO₂ in deep saline formations. Findings of the first phase (Phase I) of this investigation were presented in a topical report (Sass et al., 1999a). Preliminary results of the second phase (Phase II) experiments, now underway, have been reported elsewhere (Sass et al., 1999b; 2001). Evaluations of the suitability of the Mt. Simon formation for sequestering CO₂ and economic issues are reported by Gupta et al. (1999; 2001); Smith et al. (2001). This study is sponsored by the U.S. Department of Energy's National Energy Technology Laboratory (NETL) under a Novel Concepts project grant (Contract No. DE-AC26-98FT40418).

OBJECTIVE

The overall objectives of Phase II experiments were to determine: (1) the potential for long-term sequestration of CO₂ in deep, regional host rock formations; and (2) the effectiveness of overlying caprock as a barrier against upward migration of the injected CO₂. To meet these goals, experiments were conducted using rock samples from different potential host reservoirs and overlying rocks. In addition, pure mineral samples were used in some experimental runs to investigate specific mineralogical reactions. Due to space limitations, the scope of this paper will be limited to two types of equilibration experiments using pure minerals. Implications for more complex natural systems will be discussed in the report for Phase II being finalized at this time.

APPROACH

Experiments were conducted using an apparatus designed to simulate conditions in geologic formations deeper than 800 meters, so that hydrostatic pressure exceeds the critical pressure of CO₂ (7.375 MPa). Samples of anorthite (calcium-rich plagioclase feldspar) and glauconite (iron-rich clay) were obtained from mineral suppliers for use in these tests. Standard hydrothermal techniques were used throughout this study. Pressurized cylinders of carbon dioxide and nitrogen gases were used to control the gas composition and system pressure. Synthetic brine solutions were prepared to simulate regional compositions within the Mt. Simon formation in Ohio and Indiana. At the conclusion of the experiments, samples of the solid, liquid, and gas phases were analyzed to characterize the reactions having taken place.

PROJECT DESCRIPTION

Experimental Setup and Operation

All experiments were conducted in liter-capacity pressure vessels. The vessels were composed of Hasteloy-C material that were fitted with internal PTFE-Teflon liners for chemical inertness. Reactants consisted of pure phase solids, brine, and gas. A small amount of sodium sulfite was added immediately before closing each vessel to scavenge residual dissolved oxygen. After closure, the vessels were pressurized with CO₂ or a mixture of CO₂ and N₂. Heating wire was wrapped around each of the vessels, and thermocouple attachments allowed temperature to be controlled automatically. Figure 1 is a schematic drawing of the laboratory setup.

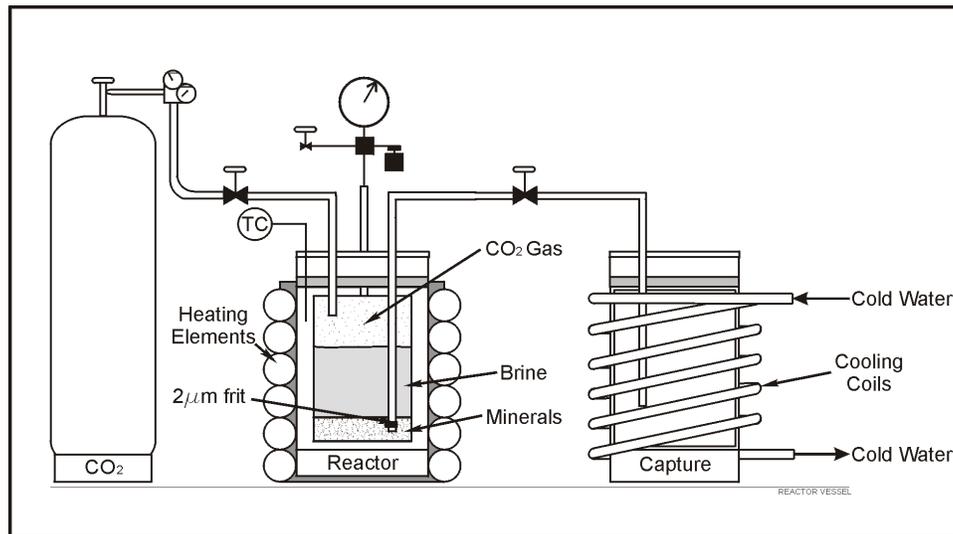


Figure 1. Schematic Drawing of Reaction Vessel.

Preparation of Solid Samples

Specimen-size quantities of anorthite and glauconite were ground in a jar mill and sieved to recover the 38 to 106- μm -size fraction. After sieving, the powders were washed in deionized water with ultrasonic agitation to remove both excess salt and extremely fine and possibly amorphous material that may have been produced by grinding. The powders then were vacuum dried at 40°C for 7 hours. A portion of each material was saved for chemical and mineralogical analysis. Prior to beginning the experiments, the solid phases were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM) with

energy dispersive spectroscopy (EDS). In addition, bulk compositions were determined by wet chemical methods. The composition of anorthite was $\text{Ca}_{0.91}\text{Na}_{0.07}\text{Al}_{1.96}\text{Fe}_{0.06}\text{Si}_{2.02}\text{O}_8$, plus trace amounts of Ti and Cr; iron was assumed to be all Fe^{II} . The composition of glauconite is approximate because of uncertainty in the oxidation state of iron. The result was $\text{Na}_{0.01}\text{K}_{0.33}\text{Ca}_{0.10}\text{Fe}_{0.56}\text{Al}_{0.41}\text{Mg}_{0.53}\text{Si}_{4.44}\text{O}_{10}(\text{OH})_2$, plus trace amounts of Cr, Ni, and P; Fe^{II} and Fe^{III} were assumed to be present in equal amounts; H_2O was not determined.

Experimental Parameters

After attaching tubing and instrumentation lines, vessels were pressurized with high-purity nitrogen gas to detect leaks. The vessels were heated and topped off with nitrogen gas or CO_2 gas to achieve a final total pressure of between 2,000 and 2,500 psi. Sensors to monitor pressure and temperature were connected and the vessels were placed on a shaker table or rocker to agitate the mixtures throughout the course of the experiments. In some runs, small amounts of gas and liquid were collected at interim times to verify the approach toward equilibrium. Table 1 lists the contents and conditions of four experiment runs that are described in this paper.

Table 1. Conditions in Pure Mineral Experiments

Experiment No.	Mineral Contents	T, P _{TOT} , P _{CO2}	Run Duration (days)
2B	Glauconite	50°C, 2,000 psi, 600 psi	30
2C	Anorthite	50°C, 2,000 psi, 600 psi	34
3G	Anorthite	150°C, 2,000 psi, 2,000 psi	30
3H	Glauconite	150°C, 2,000 psi, 2,000 psi	30

Sampling and Analysis Procedures

At the end of each experimental run, a sample of gas was extracted from the pressure vessel and the solid and solution phases were separated by siphoning liquid through a 2 μm -frit mounted inside a tube that extended to the bottom of each vessel (see Figure 1). The solutions were analyzed for total carbon, alkalinity, pH, ORP, and major and minor ions. The solids were rinsed with deionized water, dried, and then analyzed in the same manner as the unreacted samples for comparison. Routine analysis of solid phases consisted of XRD and SEM/EDS. Additional characterization was performed using x-ray photoelectron spectroscopy (XPS), which probes the top 50 to 100 \AA of surface. XPS measures elemental concentrations at the surface of mineral grains and can be useful for looking for compositional changes at mineral surfaces.

RESULTS

The following sections present preliminary results and discussion for two sets of experiments using pure mineral phases. These results should be considered preliminary at this time. A more detailed evaluation of all experimental results and comparison with geochemical simulations will be made at the conclusion of the study.

Batch Experiments

Results of the solution analyses are shown in Table 2. The initial brine compositions also are shown for comparison with the reacted mixtures. In general, the solutions analyzed at the end of the experiments were more concentrated in dissolved species, overall. The net increase in total dissolved solids could be

due to any of three factors: (1) dissolution of soluble salts that were not removed by rinsing the ground material before the tests were begun; (2) dissolution of mineral matter (primarily silicates, but may include carbonates and sulfate minerals) during the experiment; and (3) concentration of the brine as a result of evaporation from the reactor.

Table 2. Concentrations of Dissolved Species (mg/L) in Brine after Reaction with Mineral Samples

Sample ID	Brine Solution			Brine Solution		
	2	2B	2C	3	3G	3H
Experiment No.	2	2B	2C	3	3G	3H
Alkalinity	23	327	630	18	610	ND
Chloride	61,200	60,100	69,100	NA	NA	NA
Sulfate	1,080	1,825	1,300	900	600	1,650
Aluminum	ND	1.46	1.31	0.00	ND	0.00
Arsenic	0.26	0.58	0.63	0.37	0.55	0.37
Barium	0.28	0.45	0.34	0.29	0.67	0.30
Calcium	7,840	10,369	10,004	9,400	6,319	9,650
Chromium	0.04	0.06	0.20	0.03	0.06	0.04
Cobalt	0.02	0.92	1.24	0.01	0.23	0.01
Copper	0.29	0.28	0.74	0.33	1.34	0.32
Iron	0.17	4.59	19.38	0.21	117.88	0.23
Lead	0.02	0.00	0.07	0.01	0.35	0.01
Magnesium	1,286	1,873	1,568	1,310	5,560	1,390
Manganese	0.02	22.81	1.17	0.01	3.87	0.01
Nickel	0.09	6.41	8.39	0.06	5.82	0.06
Phosphorus	0.04	0.27	0.03	0.00	ND	0.00
Potassium	793.87	2,493	1,003	987	1,630	987
Scandium	0.01	0.01	0.01	0.00	0.07	0.01
Silicon	1.14	32.0	30.8	0.85	162	0.93
Sodium	22,666	28,794	30,811	24,300	31,755	24,200
Strontium	5.06	6.92	6.42	4.75	120.69	4.65
Tin	0.00	0.00	0.01	0.01	ND	0.02
Titanium	17.27	16.96	19.06	16.90	15.95	17.00
Vanadium	0.43	0.42	0.39	0.31	0.57	0.29
Yttrium	0.00	0.01	0.00	0.01	0.00	0.01
Zinc	0.16	0.90	0.36	0.07	5.97	0.07
Zirconium	0.00	0.00	0.00	0.00	0.01	0.01
pH	ND	6.28	6.11	7.31	6.28	5.35
ORP (mV)	ND	-70.9	42.1	220.1	-73.6	69

ND = Not detected; NA = Not analyzed; ORP = oxidation-reduction potential.

It is important to note that measurements of alkalinity and pH listed in Table 2 are not representative of conditions while the experiment was in progress. This is because the pressure drop upon decanting the solution causes dissolved CO₂ to volatilize and changes the distribution of carbon species in solution.

Results of vapor phase analysis by gas chromatography are shown in Table 3. In Experiment 2, the vapor consisted of approximately 20% CO₂ and 80% N₂. In Experiment 3, the vapor consisted of approximately 95% CO₂ and 5% N₂. The O₂ content was low in both sets of experiments, due to precautions taken to exclude oxygen from the system. The gas composition data were used to model the solution and thereby infer the amount of CO₂ dissolved in the liquid phase.

Table 3. Composition of Gas Phase at End of Experiments (% by Volume)

Experiment No.	Mineral Type	% CO ₂	% N ₂	% O ₂
2B	Glauconite	20.31	78.32	1.37
2C	Anorthite	21.02	77.86	1.12
3G	Anorthite	91.37	8.29	0.34
3H	Glauconite	94.95	3.11	1.94

XPS Analysis

Starting materials and reaction products were analyzed by XPS to determine whether surface composition changed as a result of the experiments. In XPS, binding energies of core shell electrons ejected by x-rays are used to identify compositional elements. Peaks in the XPS spectrum correspond to the abundance of atoms that emit photoelectrons, and are proportional to the concentration of elements in the surface region of the sample. Typically, these emissions account for the top 50 to 100 Å of the surface. For example, the silicon 2p emission occurs at approximately 100 eV in silicates. This energy can vary slightly (i.e. shift) due to the particular structure of the compound containing silicon; and this *chemical shift* effect enables XPS to differentiate elements based on local chemical environment.

Anorthite. Figure 2 compares an XPS spectrum for unreacted anorthite with a spectrum obtained after reacting a sample with CO₂ and brine for 30 days at 150 °C (Experiment 3G). In this figure, elements were identified according to the binding energy for each type of emission, which are labeled above the peaks. (A spectrum for Experiment 2C was also performed, but is not shown in Figure 2). Peaks labeled 1s and 2p are photoelectron emissions and peaks labeled KLL are Auger electron emissions. Peak intensities (height or area) were used to calculate concentrations as percentages of the total intensity.

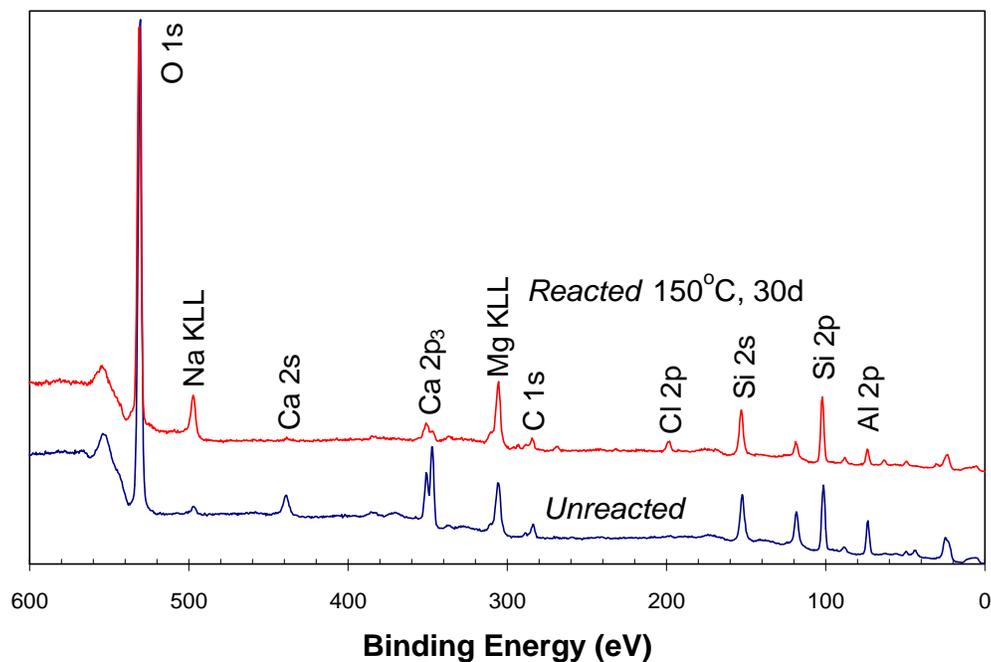
**Figure 2. Portion of the XPS Spectrum for Unreacted and Reacted Anorthite (Experiment 3G)**

Table 4 summarizes data for anorthite prior to reaction and after reacting at 150 °C for 30 days. Table 4 also lists elemental percentages for ideal anorthite of composition that is 90% pure end member of the plagioclase feldspar series and 10% albite (sodium end member), or An₉₀. Terms in the brackets next to the element symbols indicate the photoelectron emission used in the analysis.

It can be seen that all of the anorthite specimens contain 4 to 5% carbon. However, none of this carbon is in the carbonate form. Based on the binding energy of the carbon signal, this carbon is likely a hydrocarbon which could have sorbed onto particle surfaces from exposure to vacuum equipment.

Table 4. Results of XPS Analysis of Anorthite in Percent Peak Area

Sample	C[1s]	O[1s]	Na[1s]	K[2p]	Mg[1s]	Ca[2p]	Al[2p]	Si[2p]	Cl[2p]	Fe[2p3]
Ideal An ₉₀ ^(a)	0.00	61.54	0.77	0.00	0.00	6.92	14.62	16.15	0.00	0.00
Unreacted	4.98	63.46	0.65	0.00	3.42 ^(b)	5.02	8.77	12.94	0.11	0.66
30 day, 150°C	5.35	60.38	4.90	0.09	5.89 ^(b)	1.45	4.88	15.13	1.16	0.77

(a) Calculated signal area; (b) sample impurity not related to anorthite.

The sodium content of the solid increased as a result of reaction. Also, the calcium content decreased in approximately the same proportion as sodium increased. Because an increase in sodium content could result from incomplete rinsing of brine from the reacted samples, chloride also was analyzed to determine if it behaved similar to sodium. Table 4 shows that chloride was slightly higher in the two reacted samples, indicating that the specimens may have had some residual brine, but the chloride content is several factors less than the increase in sodium. This result indicates that the increase in sodium cannot be attributed entirely to residual salt. Rather, the sodium appears to be incorporated into the structure of the feldspar.

The data in Table 4 were recalculated to remove chloride, magnesium, and carbon impurities. Results are given in Table 5. Now it can be seen that wet chemical and XPS analysis of sodium and calcium in the unreacted sample are in close agreement. In comparison, the aluminum and silicon contents differ somewhat with the bulk analysis. Compared to the bulk analysis (and to the ideal structure for An₉₀), XPS results show that the unreacted sample contain excess silicon and is deficient in aluminum.

Table 5. XPS Analysis of Anorthite - Corrected for Impurities

Sample	Sodium	Calcium	Silicon	Aluminum	Iron
Unreacted ^(a)	0.07	0.91	2.03	1.96	0.06
Unreacted	0.10	0.90	2.33	1.58	0.12
30 day, 150 C	0.72	0.28	2.93	0.95	0.15

(a) Based on bulk chemical analysis of sample.

The inverse relationship between sodium and calcium was examined further by plotting the composition of the specimens against theoretical values for the anorthite-albite series. The left plot on Figure 3 shows that the sodium and calcium content for the unreacted sample falls on the theoretical curve for plagioclase at 90% anorthite and 10% albite, or An₉₀. In these plots, atomic percentages were recalculated without impurities such as carbon and chloride (as in Table 5). When sodium and calcium concentrations in the reacted specimens are plotted on the theoretical curve, the predicted composition is An₂₈ for the sample equilibrated for 30 days at 150 °C.

The relationships of the feldspar reactions depicted in Figure 3 suggests that calcium was partially replaced by sodium during the experiments, and that the extent of replacement is enhanced by higher tem-

perature. Calcium, liberated due to the reaction, is available for precipitating carbon species from solution in the form of calcium carbonate. However, no calcium carbonate was detected at the conclusion of these experiments. The absence of calcium carbonate can be explained by the pH of the solution remaining too low to stabilize a carbonate mineral. In subsequent experiments, carbonate buffer was added to control pH, and kaolinite or smectite were included with the solid components to seed the reaction. It is hoped that these measures will encourage precipitation of calcium carbonate.

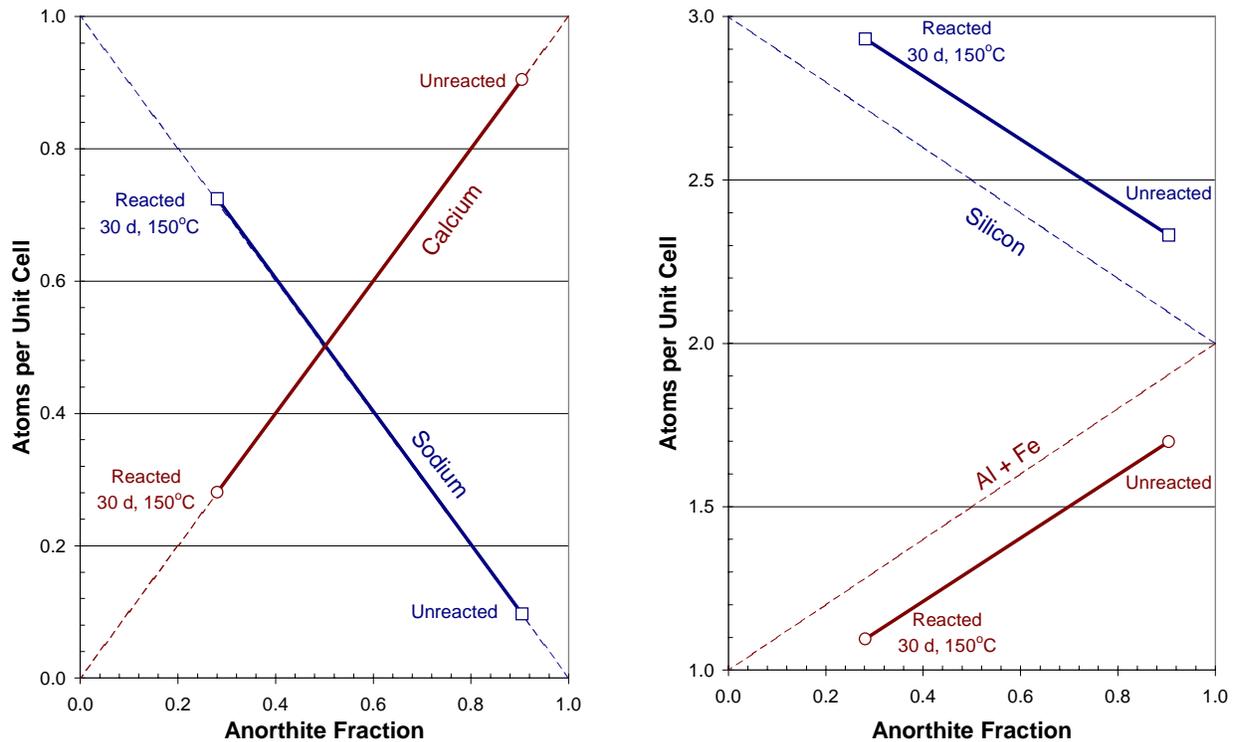


Figure 3. Change in Anorthite Composition as a Result of Mineral Equilibration Reactions (based on data in Table 5); Ideal Formulae Show by Dashed Lines.

Glaucinite. Products of experimental runs consisting of glauconite clay, brine and CO₂ also were analyzed by XPS to detect compositional changes after the reaction. As the results in Table 6 show, small but significant differences in composition were observed in the glauconite sample after the equilibration experiment. In particular, the sodium content increased substantially (after correcting for chloride), while the aluminum, magnesium and calcium content was unchanged, and potassium, iron, and silicon decreased. Glaucinite was chosen as a starting material for tests in this study because of the potential for iron to precipitate iron carbonate. Although no iron carbonate compound (siderite) was observed in the reaction products, tests will be continued to determine if siderite can be precipitated under suitable (reducing) conditions.

Table 6. Results of XPS Analysis of Glaucinite in Percent Peak Area

Sample	C[1s]	O[1s]	Na[1s]	Mg[1s]	Al[2p]	Si[2p]	Cl[2p]	K[2p]	Fe[2p3]	Ca[2p]	F[1s]
Unreacted	1.11	67.49	0.2	2.79	3.46	17.03	0.05	2.86	3.92	0.98	0.11
30 day, 150°C	2.21	65.32	1.28	2.83	3.45	16.73	0.32	2.49	3.69	1.09	0.58

APPLICATION

Experiments to verify mineral trapping show progress toward that end, but generally are too slow to be completed during short time periods (< 1 year). Surface spectroscopic techniques (e.g. XPS) indicate that elemental compositions at mineral surfaces were modified as a result of the experiments. Moreover, these changes occurred in such a way that agrees with equilibrium modeling calculations. For example, when anorthite (calcium aluminosilicate) was reacted in brine, the calcium and aluminum content at the mineral surface decreased, which is consistent with equilibrium modeling that indicates precipitation of calcium carbonate (calcite) and kaolinite (clay). This, and similar types of behavior, indicate that reaction progress was made, but that time limitations prevented reaching equilibrium.

Geochemical modeling has been used to confirm mineral dissolution behavior and to predict carbonate precipitation under equilibrium conditions. An expanded thermochemical database from Lawrence Berkley Laboratory is now being used to evaluate potential reactions involving CO₂ under geochemical conditions that could occur during carbon sequestration in deep formations. This modeling work, when completed, will provide greater insight into potential reactions that may be occurring over many years or centuries.

FUTURE ACTIVITIES

Results from the full suite of experiments being conducted will be compared with geochemical simulation data. Also, recent changes in experimental parameters are expected to speed reaction progress. For example, some experiments are being seeded with kaolinite or montmorillonite clay to help initiate the reactions. In addition, some of experiments now being conducted include a pH buffer, which is expected to stabilize pH and allow carbonate phases to precipitate more readily than in previous experiments. Addition of buffer enhances the conversion of carbonic acid to bicarbonate ion, which helps produce solid carbonates in the presence of divalent ions, such as calcium and iron. In other new experiments, rock samples with natural pyrite present are being used to test whether iron carbonate (siderite) can be formed. This series of tests is designed to show where mineral trapping by carbonates can be demonstrated in the laboratory.

REFERENCES

- Sass, B., N. Gupta, L. Smith, and E. Drescher. 1999a. *Experimental Evaluation of Chemical Sequestration of Carbon Dioxide in Deep Saline Formations*. Phase I Topical Report. Prepared by Battelle for the U.S. Department of Energy, Federal Energy Technology Center, under DOE Contract No. DE-AC26-98FT40418.
- Sass, B., N. Gupta, J. Sminchak, and P. Bergman. 1999b. Geoc hemical Modeling to Assess the Capacity of a Midwestern United States Geologic Formation for CO₂ Sequestration. *Proceedings of Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland, August 30 – September 2, 1998*.
- Sass, B., N. Gupta, J. Ickes, P. Bergman, and C. Byrer. 2001. Experimental Evaluation of Chemical Sequestration of Carbon Dioxide in Deep Saline Formations. *Proceedings of Fifth International Conference on Greenhouse Gas Control Technologies, Cairns, Australia, August 14-16, 2000*.
- Gupta, N., P. Wang, B. Sass, P. Bergman, and C. Byrer. 2001. Regional And Site-Specific Hydrogeologic Constraints on CO₂ Sequestration in the Midwestern United States Saline Formations. *Proceedings of Fifth International Conference on Greenhouse Gas Control Technologies, Cairns, Australia, August 14-16, 2000*.

Gupta, N., B. Sass, J. Sminchak, T. Naymik, and P. Bergman. 1999. Hydrodynamics of CO₂ Disposal in Deep Saline Formation in the Midwestern United States. Proceedings of Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland, August 30 - September 2, 1998.

L.A. Smith, N. Gupta, B.M. Sass, T.A. Bubenik, C. Byrer and P. Bergman. 2001. Engineering and Economic Assessment of Carbon Dioxide Sequestration in Saline Formations, *First National Conference on Carbon Sequestration*. Washington DC. May 15-17.