Use of Forced Mineral Trapping for Sequestration of CO$_2$

B. P. McGrail
Pacific Northwest National Laboratory
P.O. Box 999, MS K6-81
Richland, Washington 99352
pete.mcgrail@pnl.gov; 509-376-9193

K. P. Saripalli
Pacific Northwest National Laboratory
P.O. Box 999, MS K6-81
Richland, Washington 99352
prasad.saripalli@pnl.gov; 509-376-1667

B. M. Sass
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio 43201
sassb@battelle.org; 614-424-6315

P. F. Martin
Pacific Northwest National Laboratory
P.O. Box 999, MS P8-37
Richland, Washington 99352
paul.martin@pnl.gov; 509-376-2591

S. L. Bryant
University of Texas
Austin, Texas 78712
sbryant@ticam.utexas.edu; 512-475-8631

Introduction

Among the options being considered to help mitigate anthropogenic CO$_2$ emissions is carbon sequestration in depleted oil or gas wells, coal seams, and deep underground saline formations. One of the uncertainties that must be addressed with respect to geologic sequestration is the long-term risk associated with storage of large quantities of CO$_2$ in the subsurface. Rapid release of CO$_2$ could occur from reservoir failure due to seismic events, overpressurization, or other mechanical failures. In addition to the consequences of releasing the stored CO$_2$ back into the atmosphere, a potential asphyxiation risk to a local population exists because CO$_2$ is heavier than air, so it tends to stay near ground level until dispersed. Holloway (HOLLOWAY, 1997) discusses several fatalities that have resulted from catastrophic but naturally occurring CO$_2$ releases.

Mineral trapping, the chemical binding of CO$_2$ by chemical reaction with calcium and magnesium to form stable carbonates, is often discussed as a permanent carbon sequestration option (HERZOG et al., 1993; BACHU et al., 1994;

HITCHON, 1996; KOJIMA et al., 1997). However, mineral-trapping processes that rely on dissolution of minerals in the host rock to supply the required Ca and Mg may require thousands of years to complete because of the slow dissolution kinetics of the primary host minerals. In addition, injection and pressurization with CO$_2$ naturally produces carbonic acid. Because the solubility of calcite increases rapidly at pH<8, net dissolution, not precipitation of calcite, will occur as a result of CO$_2$ injection. Thus, natural mineral trapping is an unlikely mechanism for permanently sequestering significant amounts of CO$_2$. A simple, low-cost method is needed to establish a thermodynamically favorable environment for mineral trapping in the host formation.

In the U.S., hundreds of millions of tons of construction/demolition (C&D) waste are generated per year (LUND, 1993). Over 60% of the mass content of typical demolition debris is concrete (LUND, 1993). Lack of established markets and recycling facilities results in much of this material being landfilled in many parts of the country. Because the principal constituent in

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concrete is portlandite [Ca(OH$_2$)], C&D waste represents a potentially large source of alkalinity. Rain or irrigation water reacting with crushed concrete would provide a source of Ca(OH)$_2$ for use in conditioning shallow terrestrial or deep geologic reservoir pore water to enhance formation of carbonate minerals.

In this paper, we describe a novel set of experiments and modeling simulations to examine the feasibility of pore water chemical conditioning for permanent sequestration of CO$_2$. First, we discuss issues associated with forced mineral trapping in the subsurface.

SLIP Concept

To induce forced mineral trapping, an alkaline solution derived from reaction with reclaimed C&D waste, principally Ca(OH)$_2$, is injected into the host formation that is then overpressured with CO$_2$(g). Supersaturation of the aqueous phase with respect to calcite will result in precipitation of this mineral. However, precipitation of calcite will inherently alter the pore structure of the rock, along with its hydraulic properties. Unusual coupled feedback effects on flow and transport have been reported for similar systems (RENARD et al., 1998; STEEFEL and LICHTNER, 1998; MCGRAIL et al., 1999a). The coupled flow and chemical reaction processes associated with forced mineral trapping could easily lead to formation damage and well blowout (SARIPALLI et al., 2000) with concomitant poor utilization of reservoir capacity for CO$_2$ sequestration. An injection strategy is needed that can overcome these difficulties.

SLiding In situ Precipitation (SLIP) is a concept for controlling the extent and location of a precipitation front generated from chemically reactive flows in porous media. SLIP takes advantage of the special properties of dissolution/precipitation waves that form in advection-dominated systems (BRYANT et al., 1987). Dissolution/precipitation in chemically reactive flows induces shock discontinuities that have

several important characteristics. A particularly useful characteristic for SLIP is the downstream equilibrium condition (DEC), where the solute concentrations downstream of a precipitation front satisfy the equilibrium solubility product for the solid precipitate, regardless of whether or not the precipitate is actually present downstream (BRYANT et al., 1987). The DEC is important because it provides a theoretical basis for repositioning a precipitation front in a dynamic system without inducing dissolution of the target mineral downstream of the front.

Theoretical Analysis

To illustrate the basic concept of SLIP, a simple reactive chemical transport simulation was performed. We consider the following set of chemical reactions

$$CO_2(g) + H_2O = H^+ + HCO_3^- \qquad K_1 = 10^{-7.8} \quad (1)$$

$$H^+ + OH^- = H_2O \qquad K_2 = 10^{14} \quad (2)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad K_3 = 10^{1.9} \quad (3)$$

where the K_i values are the equilibrium constants for each reaction. Equations (1) and (2) are considered fast reactions and so are always in a local state of equilibrium. The calcite dissolution/precipitation reaction is considered kinetically controlled, according to a simple rate law

$$r = k_o A_3 H(-A_3) \qquad (4)$$

where r is the dissolution/precipitation rate, k_o is a rate constant, $H(-A_3)$ is the Heaviside step function, and A_3 is a chemical affinity term given by

$$A_3 = 1 - Q / K_3 \qquad (5)$$

where Q is the ion activity product that for this example is simply $Q = [Ca^{2+}][HCO_3^-]/[H^+]$. We consider a 1-D flow and advective transport problem (neglecting dispersion) where a 0.02M Ca(OH)$_2$ solution and pure CO$_2$(g) are injected into a uniform porous medium with porosity of

0.5 and volumetric water content of 0.25 (50% water saturated). The pertinent boundary conditions are:

$$v_1[Ca(OH)_2] = f_1, \quad x = 0, L \qquad (6)$$

$$v_2[CO_2(g)] = f_2, \quad x = 0, L \qquad (7)$$

where v_n is the pore velocity, f_n is the injection rate, and L is the length of the porous medium. The boundary conditions (6) and (7) simply state the $Ca(OH)_2$ solution and $CO_2(g)$ are injected at a constant rate at either end of the porous medium. The modeling was conducted with a modified version of the INVERTS code (McGrail, 2001).

Single-Well Injection

Single-well injection of the $Ca(OH)_2$ solution and $CO_2(g)$ was simulated with INVERTS by injecting both reactants at the $x = 0$ boundary. The injection rate of the $Ca(OH)_2$ solution was held constant while the CO_2 injection rate was varied from 1.0 to 0.25 (arbitrary units). The simulation time was selected so the $Ca(OH)_2$ wave front traversed ¾ of the length of the porous medium. The calcite precipitation rate constant (k_o) was selected so the Damköhler number (based on a fixed inlet Ca concentration) was

40; a high Damköhler number ensures that precipitation is rapid relative to the rate of mass transport in the system.

The results in Figure 1 show how the Ca^{2+} and HCO_3^- concentration change as the CO_2 injection rate increased relative to the injection rate of $Ca(OH)_2$. As shown in Figure 2, calcite is predicted to be precipitating only in a very narrow region near the injection point. Yet, the solution composition (Figure 1) remains in equilibrium with calcite downstream of the precipitation front, a clear illustration of the DEC discussed previously. Because of the highly localized nature of the precipitation front, the single-point injection strategy would result in very poor utilization of the available porosity for mineral trapping and would plug the area of review around the injection well very rapidly.

Counter-Flow Injection

An alternative to the single-point injection strategy is to inject the reactants at different locations. This counter-flow injection strategy establishes a completely different behavior when the two wave fronts interact, as shown in Figure 3. Now, increasing the rate of $CO_2(g)$ injection displaces the location of the calcite precipitation along the direction of CO_2 flow but
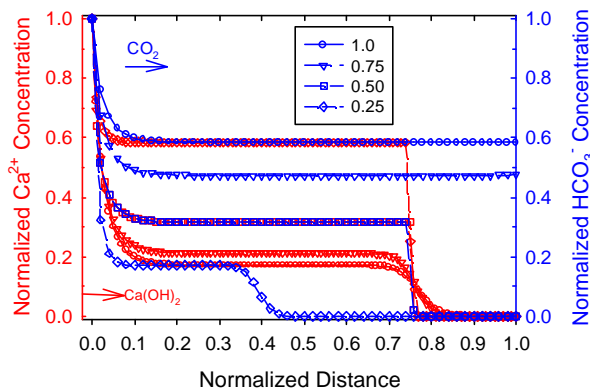

Figure 1. Normalized Concentration of Ca^{2+} and HCO_3^- in One-Dimensional Simulation of Single Point Injection of Alkaline $Ca(OH)_2$ Solution and $CO_2(g)$. Injection rate of $Ca(OH)_2$ was held constant while the $CO_2(g)$ injection rate was varied from 1.0 to 0.25 (arbitrary units).
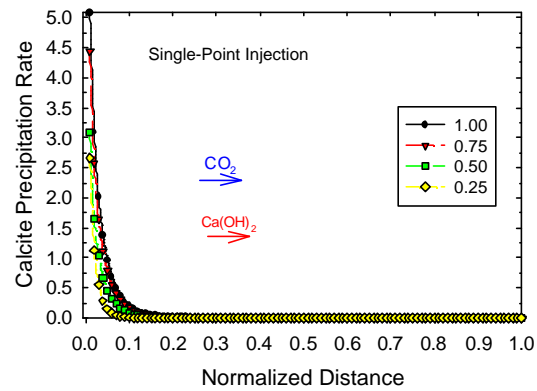

Figure 2. Precipitation Rate (Arbitrary Units) of Calcite as a Function of Distance from the Injection Point using Single-Point Injection. Injection rate of $Ca(OH)_2$ was held constant while the $CO_2(g)$ injection rate was varied from 1.0 to 0.25 (arbitrary units).
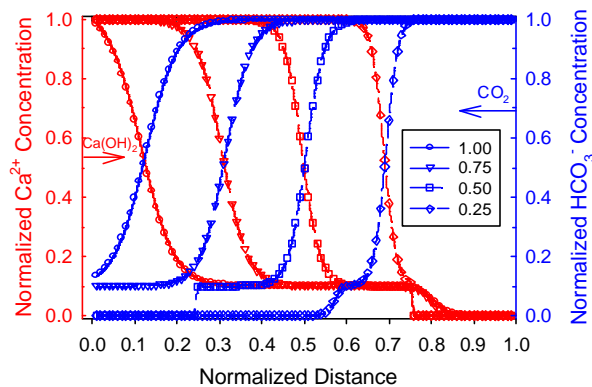
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Figure 3. Normalized Concentration of Ca^{2+} and HCO_3^- in 1-D Simulation of Counter-Flow Injection of Alkaline $Ca(OH)_2$ Solution and $CO_2(g)$. Injection rate of $Ca(OH)_2$ was held constant while the $CO_2(g)$ injection rate was varied from 1.0 to 0.25 (arbitrary units).

Figure 4. Precipitation Rate (Arbitrary Units) of Calcite as a Function of Distance from the Injection Point using Counter-Flow Injection. Injection rate of $Ca(OH)_2$ was held constant while the $CO_2(g)$ injection rate was varied from 1.0 to 0.25 (arbitrary units).

counter to the flow of the $Ca(OH)_2$ solution. Also, the DEC is maintained *in both* directions upstream and downstream (relative to one of the reactants). This characteristic is important because it is possible to slide the precipitation front, as shown in Figure 4, in either direction by changing the injection parameters without destabilizing the calcite that has already precipitated. Finally, Figure 4 shows how the precipitation front broadens as the relative rate of CO_2 injection increases. This result is a consequence of the kinetic constraint on the precipitation of calcite and the decrease in Damköhler number as the injection rate is increased. Relative to the single-point injection, the ability to slide the precipitation front to different locations suggests the strategy could be successfully used to optimize utilization of the available pore space for carbonate mineral trapping.

PUF Experiments

To validate the model analysis discussed in the previous section, a set of pressurized unsaturated flow (PUF) experiments was conducted. The PUF apparatus is a patented (MCGRAIL et al., 1999b) device that is used extensively at PNNL to study chemically reactive flow processes in unsaturated porous media (MCGRAIL et al.,
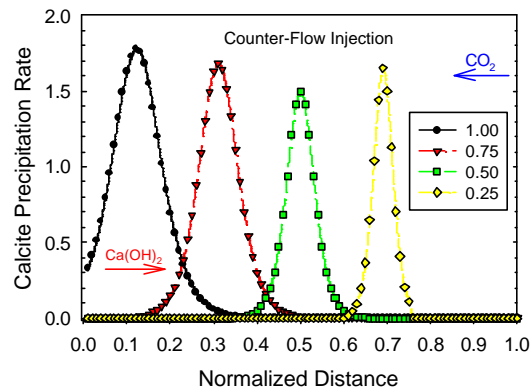
1997). The basic test apparatus consists of a column packed with crushed test material (or materials) of a known particle size and density, a computer data acquisition and control system, fluid pump, and electronic sensors, as illustrated in Figure 5. A porous titanium plate with nominal pore size of 0.2 µm is sealed in the bottom of the column to ensure an adequate pressure differential for the conductance of fluid while operating under unsaturated conditions (WIERENGA et al., 1993). Titanium was chosen because it is highly corrosion resistant and has excellent wetting properties. When water saturated, the porous plate allows water, but not air, to flow through it, as long as the applied pressure differential does not exceed the air entry relief pressure, or bubble pressure, of the plate.

The computer control system runs LabVIEW™ (National Instruments Corporation, Austin, Texas) software for logging test data to disk from several thermocouples, pressure sensors, and inline sensors for effluent pH and conductivity. The column can be placed on an electronic balance (as shown in Figure 5) or suspended from an electronic strain gauge to accurately track water mass balance and saturation level.
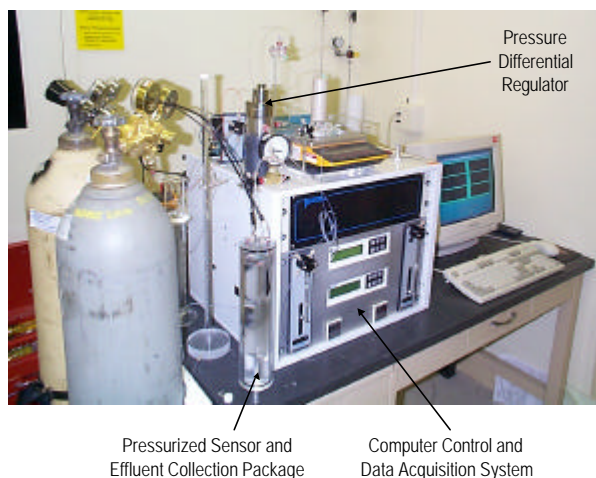
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Figure 5. Photo of PUF System Configured for Carbon Sequestration Studies. The effluent collection, pH, and electrical conductivity sensors are housed in a separate instrument package pressurized with helium.

An important modification to the PUF system was needed to conduct CO_2 injection experiments. Injection pressures on the order of 100 to 200 psig are desired but the applied pressure *differential* across the porous plate in the column cannot exceed its bubble pressure of approximately 7 psig. To compensate, we developed the pressure differential control system shown in Figure 5. Here, the pH, electrical conductivity sensors, and effluent collection vial are all housed in a chamber that is pressurized with helium. He is used to prevent modification of the effluent chemistry that would occur at high CO_2 pressures. A differential regulator maintains the pressure differential between the PUF column and the sensor/effluent instrument package within the 7 psi bubble pressure limit. Consequently, CO_2 injection experiments can be conducted at realistic operating pressures and temperatures.

Single-Point Injection Experiment

In this experiment, both $CO_2(g)$ and a 0.02M $Ca(OH)_2$ solution were injected at the top of a column (see Figure 6) filled with a quartz sand

Figure 6. Close Up Photo of PUF Column After 72 h of Injection with $Ca(OH)_2$ and $CO_2(g)$. Note very small blue area just under the $Ca(OH)_2$ inlet that defines the calcite precipitation front.

of nominal 425 to 250 µm particle size. The $Ca(OH)_2$ solution was doped with a cresol red - thymol blue pH indicator that has a critical pH for color change of about pH 9. After 74 h of injection, visual observations showed the blue color (indicating alkaline pH) remained within a few mm of the CO_2 injection port. The blue area defines the precipitation front because it defines the location where the injected base has not been neutralized by the injected CO_2 via reaction (1). An x-ray microtomograph of the column showed a few cm^3 area near the CO_2 injector with higher density than other areas in the column. This observation was confirmed after dismantling the column; as shown in Figure 7, significant deposits of calcite were found near the top of the column but no precipitate was observed in samples taken at other locations. These findings directly validate the predictions for the single-point injection calculations shown in Figure 2.

Counter-Flow Injection Experiment

A similar PUF experiment was performed as previously described except the CO_2 injection point was relocated to the bottom of the column, just above the porous plate. Figure 8 shows the
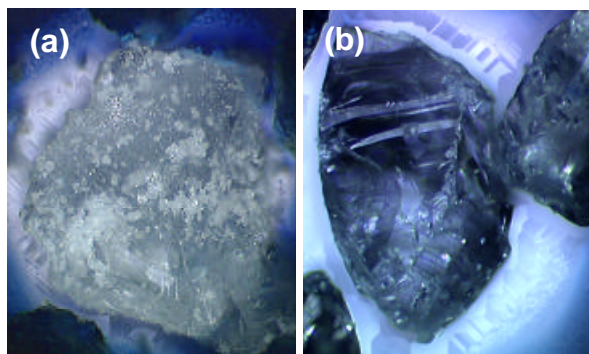
Figure 7. Optical Photos of Quartz Grains Removed from Top (a) and Bottom (b) of Column After PUF Test. Note extensive calcite precipitation on quartz grain near top of the column.

Figure 8. Close-Up Photo of PUF Column With CO_2(g) injection rate of 0.1 µmol/h (a) versus 0.2 µmol/h (b). Note the shift in position of the blue area that defines the calcite precipitation front.

response of the calcite precipitation front to a 2X change in the CO_2(g) injection rate. At the higher injection rate, the precipitation front retreats toward the top of the column, in exact accord with the model predictions shown in Figure 4.

Controlling the location of the precipitation front via modifying the CO_2 injection rate is anticipated to be the preferred approach. This is because of the much higher permeability and transport rate for gases as compared with liquids. As the formation porosity declines with increasing loading of calcite, the effect on the flow and transport of CO_2(g) will be significantly less than that on the alkaline injection fluid.

Conclusion

Reactive transport calculations of a sliding in situ precipitation (SLIP) concept were validated with a set of pressurized unsaturated flow (PUF) experiments. A counter-flow injection strategy was shown to be very effective in controlling the location of a calcite precipitation front and thus could be used to maximize utilization of reservoir capacity for permanent carbon sequestration via mineral trapping. Further work is needed to examine coupled feedback mechanisms on liquid
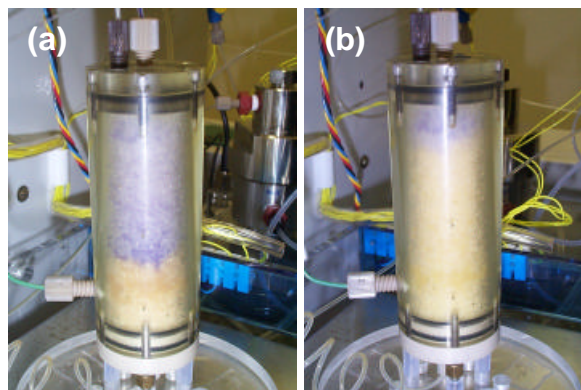
and gas flow as the permeability and pore structure of the porous medium will change significantly during the process. Work is underway to extend the modeling and experiments to investigate 2-D flow and transport processes, which may respond differently than the present 1-D analysis would suggest.

Although we have focused on the precipitation of calcite for forced mineral trapping, the technique may also work with other carbonate minerals. For example, injection of reducing stack gas impurities, such as SO_2, along with the CO_2 could be used to reduce the oxidation states of transition metals and precipitate insoluble carbonates. Iron-rich minerals, such as glauconitic clay and hematite, contain iron predominantly in the ferric state. Reduction of iron to the ferrous state could help bind carbon in the form of ferrous carbonate (siderite). Another example is forming manganese carbonate (rhodochrosite) by the reduction of manganese from manganese-bearing minerals in higher oxidation states. This electrochemical type of forced mineral trapping could be applied in formations rich in iron or manganese bearing minerals.

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