A Methodology for Measuring the Rate of Reaction of CO_2 with Brine-Rock Mixtures

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Introduction

Storage of carbon dioxide in deep, porous, and permeable reservoir rocks is one of the most promising technologies for reducing emissions of greenhouse gases to the atmosphere. Although oil and gas reservoirs are a sensible first step for sequestration of carbon dioxide in geologic formations, their total storage capacity is small compared to storage needs and their distribution is concentrated far from most power-plant sources of carbon dioxide emissions (Bergman and Winter, 1997; Bergman and Winter, 1995). Deep saline aquifers have the largest potential storage capacity for carbon dioxide because they are wide spread (Bergman and Winter, 1995) and, in contrast to oil and gas reservoirs, may not require special structural and stratigraphic trap geometries (Gunter *et al* , 1996). Instead, carbon dioxide can be stored hydrodynamically in the formation waters for tens of thousands of years and longer. In addition, mineral trapping, which involves a series of interactions between the formation mineralogy and carbon dioxide-enriched formation waters, can convert carbon dioxide to an immobile and harmless mineral form that will be stored for millions to hundreds of millions of years.

This research is part of an interdisciplinary, collaborative study of the Rose Run Formation of eastern Ohio in order to evaluate the potential of this formation to sequester carbon dioxide emissions. In addition to containing oil and gas reservoirs that may be suitable for CO_2 sequestration, the Rose Run Formation has a deep saline aquifer that is widespread across eastern Ohio. Regional flow in the Rose Run Formation is down dip (Gupta and Bair, 1997), as preferred for hydrodynamic trapping. In addition, the formation mineralogy may be appropriate for large-scale mineral trapping. Eventually, carbon dioxide injection could be expanded to make use of the Rose Run Formation's aquifer storage capacity.

One of the major concerns for carbon dioxide sequestration in saline aquifers is the impact of mineral-brine-CO_2 reactions on the storage capacity of the formation. The principle types of mineral-brine-CO_2 reactions can be predicted relatively well assuming sufficient reaction time to achieve equilibrium conditions. The actual kinetics of mineral-brine-CO_2 reactions remains poorly understood, however. Since fluid flow and fluid rock interactions are dynamic processes, kinematically determined rates of reaction will be very important to determining the localization of mineral dissolution and precipitation, and the extent of mineral trapping.
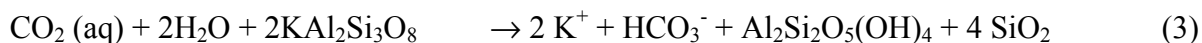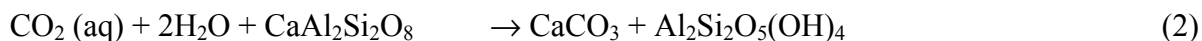
Objective

This research aims to investigate the kinds and rates of mineral-brine-CO_2 reactions expected for the Rose Run Formation and the overlying aquitard. Laboratory experiments with representative mineral samples and carbon dioxide-saturated brines will investigate the mineral reactions for appropriate temperature and pressure conditions. Experimental design will emphasize constraining rates of reactions and analyses will exploit reaction-driven changes in carbon and oxygen isotope and elemental compositions to quantify reaction rates. Ultimately, these experimental reaction rates along with field work to determine mineralogical and textural data will be incorporated into thermodynamic and kinetic geochemical models to predict mineral reactions, masses of carbon dioxide sequestration, and the time constraints for the reactions.

This poster describes the development of a laboratory apparatus and method for measuring the rates of reaction of CO_2 with brine-rock mixtures.
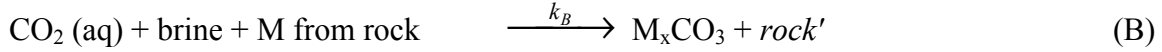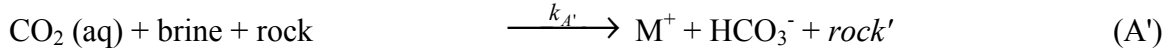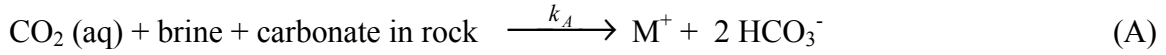
Approach

Laboratory experiments will investigate reactions between representative samples of the Rose Run Formation or the overlying aquitard, and carbon dioxide-saturated natural and synthetic brines. Current research focuses on finalizing the design and setting up the experimental apparatus. After that additional apparatus can be built and modified as needed. Initial experiments will focus on ground samples in order to constrain carbon dioxide reaction kinetics and determine reaction rates for the bulk mineralogy. Later experiments will use intact rock plugs and will study the effects of intra-sample comositional and textural heterogeneity.

Experimental measurement of CO_2 reaction kinetics: The goal of the first phase of experiments is to determine the rate of reaction of CO_2 in contact with a mixture of brine and powdered rock. The literature has identified three model reactions:

$$CO_2 \text{ (aq)} + H_2O + CaCO_3 \rightarrow Ca^+ + 2\ HCO_3^- \tag{1}$$

$$CO_2 \text{ (aq)} + 2H_2O + CaAl_2Si_2O_8 \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 \tag{2}$$

$$CO_2 \text{ (aq)} + 2H_2O + 2KAl_2Si_3O_8 \rightarrow 2\ K^+ + HCO_3^- + Al_2Si_2O_5(OH)_4 + 4\ SiO_2 \tag{3}$$

To gain more practical information, our experiments will extend this research by determining the rate of reaction of these 3 generalized mechanisms using real rock samples rather than model minerals. Generalizing these three reactions yields:

$$CO_2 \text{ (aq) + brine + carbonate in rock} \xrightarrow{k_A} M^+ + 2\ HCO_3^- \qquad (A)$$

$$CO_2 \text{ (aq) + brine + rock} \xrightarrow{k_{A'}} M^+ + HCO_3^- + rock' \qquad (A')$$

$$CO_2 \text{ (aq) + brine + M from rock} \xrightarrow{k_B} M_xCO_3 + rock' \qquad (B)$$

where M and M^+ = metal and metal ion respectively and *rock'* = acid modified rock. Reactions A and A' sequester CO_2 as aqueous HCO_3^- ion while Reaction B sequesters CO_2 as carbonate solid. Note that the above reactions are overall reactions that ignore the intermediate step of H_2CO_3 acid formation.

By assuming the reaction rates are proportional to CO_2 concentration in the brine (C_{CO2} [=] moles/cm^3) and the amount of rock sample (m [=] g), we can write the overall rate law as the sum of the above rates:

$$r_{CO2} = - (k_A + k_B + k_{A'})\ C_{CO2}\ m \qquad (4)$$

where r_{CO2} = rate of disappearance of CO_2 (moles/cm^3 of brine s).

To determine the rate constants for the individual reactions requires several different measurements. The overall rate of carbon dioxide uptake will be determined by measuring the overall rate of disappearance of CO_2 from the reactor. The relative amounts of the HCO_3^- reactions ($k_A + k_{A'}$) versus the M_xCO_3 reaction (k_B) will be determined by measuring the amount of HCO_3^- appearing in the brine and comparing it to the overall loss rate (k_{tot}). Finally, we will use isotopic analysis to distinguish between Reaction A and A'. This analysis is based on the fact that the rock has a different $^{13}C/^{12}C$ ratio than the gaseous CO_2 as described by the factor $\delta^{13}C$:

$$1\ \delta^{13}C = \frac{\left(^{13}C/^{12}C\right)_{sample} - \left(^{13}C/^{12}C\right)_{s\ tan\ dard}}{\left(^{13}C/^{12}C\right)_{s\ tan\ dard}} \times 1000 \qquad (5)$$

Note that in Reaction A, half of the HCO_3^- ions comes from CO_2 (aq) while half comes from the carbonate in the rock (see Reaction 1 above). In contrast, Reaction A' generates HCO_3^- exclusively from CO_2 (aq). Since the rock ($\delta^{13}C = 0$) is isotopically enriched in ^{13}C compared to CO_2 in the atmosphere ($\delta^{13}C = -7$; Anderson and Arthur, 1983), we can measure $\delta^{13}C$ in the HCO_3^- from the brine and use that information to infer the relative magnitudes of Reaction A and A'. CO_2 derived from coal and other organic matter ($\delta^{13}C = -25$) has an even greater disparity from carbonate carbon and could be used in a similar manner to monitor rates of reaction in the vicinity of an injection site. In addition to the above rate measurements, other analyses will be performed to determine changes in metal ion stoichiometry in the brine in order to constrain what phases are dissolving and precipitating.

Results

Review of geochemical reactions involving CO_2 – A few studies have examined the reactions between complex natural samples and carbon dioxide-saturated brines for purposes of evaluating

mineral trapping reactions. Sass et al (1999) conducted an experiment on a ground, sieved, and washed sample of sandstone from Ohio's Mount Simon Formation. The Mount Simon Formation is a quartz- and potassium feldspar-dominated sandstone with minor amounts of carbonate and clay. Sass *et al* (1999) ran a batch experiment by allowing carbon dioxide saturated synthetic brine to react with the sample for 7 days at a pressure of 800 psi and 110 ˚C. At the end of the experiment, they analyzed the liquid solution for cations and anions. They found increased levels of calcium, magnesium, and carbonate in solution, which they interpreted as evidence for dissolution of dolomite. They interpreted decreased brine concentrations of calcium and sulfate as evidence for anhydrite precipitation. Based on numerical modeling they concluded that dolomite and anhydrite reached equilibrium during the experimental run. Due to the slow kinetic rates of silicate reactions and the short runtime of the experiment, evidence of silicate mineral reactions was indiscernible.

Pearce *et al* (1996) carried out longer run-time experiments on a variety of rock types from the North Sea and did find evidence for silicate dissolution. Samples included subarkoses, arkoses, mudstones, and anhydrite. Pearce *et al* ran batch experiments in which they allowed the fluid to equilibrate with an unaltered plug of rock sample at 80 ˚C and 200 bar pressure for either 3 or 8 months. They also ran core flood experiments on the sandstone samples, forcing carbon dioxide saturated synthetic brine to pass through sandstone plugs. Anhydrite samples were severely corroded by the batch experiments, increasing porosity up to 50%. Batch experiments on mudstone featured complete dissolution of any carbonate present and disintegration of the mudstone. K-feldspars in both batch and core-flood experiments on sandstone were also corroded by interaction with carbon dioxide saturated brines. Corrosion during the experiments was concentrated on K-feldspar minerals that had already been corroded during diagenesis. Secondary clay mineral precipitation during the experiment was associated with the K-feldspar dissolution.

There is very little literature specifically examining the reaction rate as a function of CO_2 partial pressure. Lebrón and Suarez (1998) performed an experimental study to develop a model for the precipitation rate of calcite under varying CO_2 partial pressures. These authors performed their experiments at partial pressures of CO_2 ranging from 0.035 – 10 kPa. As expected, the precipitation rate of calcite increased as partial pressure of CO_2 increased. This is undoubtedly due to the fact that increasing the partial pressure of CO_2 decreases the solution pH and increases the ionic strength which strongly influence nucleation of new calcite crystals.

Review of high pressure reactor designs – Previous work on geochemical measurements at high pressure are somewhat limited. In general, these high pressure reactors are designed to meet specific needs of the experiment and are generally autoclave type reactors. For example, Jonasson *et al* (1996) studied carbonate precipitation in the presence of phosphonates in a high pressure autoclave fitted with windows for *in situ* light scattering. The autoclave consisted of a 250 cm^3 Hastelloy vessel equipped with 0.25" openings for the sapphire windows and fiber optic fittings (Parr Instrument Company). The head assembly included ports for a rupture disc, gas release valve, a gas inlet/liquid sampling valve with dip tube, and a thermowell. The seals were either metal or teflon. The autoclave is rated for up to 300 ˚C and 5400 psi. Posey-Dowty *et al* (1986) also used an autoclave design to perform kinetic studies of mineral-water interactions in hydrothermal systems. Their system was a circulating apparatus consisting of a tubular autoclave with flow circulated by HPLC pumps. The reaction vessels were constructed from 316 stainless

steel, titanium, or other corrosion resistant alloys with volumes ranging from tens to hundreds of cm^3. The apparatus can be operated in either the plug-flow or well-mixed regimes. The operating conditions varied from standard conditions to 350 °C and 140 bars with flow rates 0.5 to 320 cm^3/hr.

On the other hand, there is at least one instance of a purely plug flow reactor (PFR) system. Johnson *et al* (1998) have performed dissolution/precipitation experiments on crushed quartz and tuff using a commercial high-temperature PFR manufactured by Coretest Systems, Mountain View, CA. The reactor consisted of a titanium tube 30 cm length, 0.66 cm diameter. High operating temperatures (up to 250 °C) were reached using a three-zone furnace and controller. A high-pressure two-piston metering flow pump produced the flow in the reactor and the operating pressure is ≤ 300 atm.

Current reactor design: We have designed a low cost reactor so that multiple reactors can be constructed and run in parallel. The reactor consists of a simple ¾ inch tube (316 stainless steel) connected to a pressure gauge and a series of valves (Figure app1). The main reactor tube is 15.2 inches long producing a nominal volume 100 cm^3. At one end of the tube, there is an elbow leading to a 304 stainless steel pressure gauge while the other end of the tube is fitted with a Swagelok reducing union, decreasing the tube diameter from 3/4 inch to 1/4 inch. The smaller diameter tubing is necessary to create a small sampling volume. A ball valve (Whitney) and a stem valve (Whitney) are separated by 1.6 inches of 1/4 inch tubing, thus creating a sample capture volume of 1 cm^3. A Popper luer-lock connector is attached to the stem valve. Sampling is performed by attaching an SGE gas-tight luer-lock syringe to the luer connector and slowly flashing the sample into a syringe by way of the stem valve.

For temperature control, the main tube is wrapped with an Omegalux rope heater, which is held in place with a wire screen. For insulation, polyethylene foam pipe insulation (3/8 inch thick) surrounds the heating rope and wire screen. We manually set the temperature of the reactor using a type K thermocouple (0.020 inch) and vary the power for the heater through to a household dimmer switch. The reactor is mounted horizontally in order to slosh the three phases together to maintain uniform mixing. Agitation is provided by daily shaking the reaction vessel manually.

Nominal operating pressures and temperatures of the system are 65 atm and 75 °C although the pressure and temperature can range up to 150 atm and 150 °C, respectively. At these conditions, the CO_2 is supercritical with a density of ~ 0.22 g/cm^3 while the natural and synthetic brines have a variable density > 1 g/cm^3. Preliminary measurements will focus on crushed rock samples to minimize mass transfer effects between the brine and solids, but future rate measurements will include core samples. The brine mixture is prepared from artificial seawater (Instant Ocean manufactured by Aquarium Systems). The mineral samples come from Wards Scientific while the CO_2 is commercial grade gas from Praxair.

Sampling: The reactor experiments will last 8-12 weeks, and we will withdraw samples of both the CO_2 and brine at weekly intervals. Both fluid samples will be captured between the double valves (see Figure 1) and then released into a sample bulb at 1 atm for analysis. In case of the brine samples, there is significant CO_2 dissolved in the brine (~ 45 mg CO_2 per g water) which will also be released when de-pressurized to 1 atm.

Rather than use pure CO_2 to pressurize the reactor initially, we will use a mixture of 10-50%

Ar) in CO_2. Using Ar/CO_2 mixtures has two advantages: 1) we can control the CO_2 partial pressure independently of total pressure (i.e., effective depth), and 2) the Ar acts as an internal standard for measuring CO_2 consumption (actinometry). Since the reactions only consume CO_2, subtle changes in the CO_2/Ar ratio as determined by the mass spectrometry can be converted into a total CO_2 loss rate without worrying about sample size variations.

A blank run without rock will serve as a control for the above experiments. The blank run will identify if there is any trace contamination of the brine with metal ions from the stainless tubing.

Rate analyses: Treating the reactor as a batch system, a CO_2 mole balance yields the following:

$$r_{CO2} V_{brine} = \frac{d}{dt}\left[N_{brine} + N_{gas}\right] \tag{6}$$

where r_{CO2} appears in Equation 4, V_{brine} = volume of the brine (cm^3), N_{brine} = moles of CO_2 in the brine, and N_{gas} = moles of CO_2 in the gas. We are presuming that the mixing eliminates any mass transfer resistance among the supercritical CO_2, the brine, and the rock phases. Looking closely at the expression for r_{CO2}, we find that

$$r_{CO2} = -k_{tot} C_{CO2}\, m = -k_{tot}\left[\frac{N_{brine}}{V_{brine}}\right] m \tag{7}$$

By sampling both the brine and the gas at various times, we can determine the fractional amount of CO_2 remaining in the reactor (N_{brine} and N_{gas}). We can thus regress the data to directly determine k_{tot} using a least square method either using the differential equation above or its integral form.

A similar mole balance on the HCO_3^- ion yields the expression

$$(k_A + k_{A'})\left[\frac{N_{HCO3}}{V_{brine}}\right] m V_{brine} = \frac{d[N_{HCO3}]}{dt} \tag{8}$$

which may be integrated directly to relate the rise in HCO_3^- to $(k_A + k_{A'})$. Keeping track of the ^{13}C in the HCO_3^- ion and a similar mole balance on ^{13}C allows us to determine k_A separately.

For simplicity of presentation, the above analyses have assumed irreversible reactions, but including the reverse reactions is straightforward. The rate constants for the reverse reactions come directly from thermodynamic data from the literature. Even in the presence of significant reverse reactions, we also determine the forward rate constants using the method of initial rates (Fogler, 1999). The above experiments will be implemented using "design of experiments" approaches.

Future Activities

Year 1: Build and test experimental apparatus, and develop and refine analytical techniques for measuring mineral-fluid reactions. Carry out experiments on simple single mineral-brine mixtures varying brine composition, temperature, pCO_2 and pH.

- Literature review of experimental design and reaction rate constants.
- Construct and test prototype apparatus.
- Experiments on pure, single and dual phase mineral powders at extremes of experimental conditions to determine sensitivity to pH, temperature, brine composition, sample composition, and pCO_2.
- Test and calibrate analytical techniques, including analyses of stable isotopes, anions, cations, and microscopy for identifying dissolution, precipitation, and ion exchange reactions.
- Demonstrate simultaneous silicate dissolution and carbonate precipitation.

Year 2: Experiments on mineral powders of simple, prescribed multiphase composition and on representative rock powders varying brine composition, temperature, pCO_2 and pH.

- Construction of additional experimental setups for multiple simultaneous experiments.
- Experiments on multiphase mineral powders at end member pH, temperature, brine composition, and pCO_2.
- Begin experiments on representative Rose Run and Black River rock powders and brine compositions.
- Isotope, anion, cation, and microscopy documentation of mineral-fluid reactions.

Year 3: Continue laboratory experiments on different Rose Run sample types, brine compositions, and temperatures to determine reactions and reaction rates for different sample types. Design and build apparatus for flow-through experiments on in-tact rocks samples.

- Experiments on representative Rose Run and Black River rock powders at realistic brine compositions, pressure conditions, and over a range of temperature and pCO_2 in order to determine Arrhenius parameters and reaction order.
- Isotope, anion, cation, and microscopy studies of mineral-fluid reactions to determine the branching ratio of CO_2 sequestration reactions: how much as dissolved CO_2, how much as HCO_3 anion, how much as solid carbonates (or other minerals).
- Modify and construct experimental design for plug flow-through experiments.

Year 4: Flow-through laboratory experiments on in-tact Rose Run sample to investigate mass-transport effects on mineral –fluid reactions.

- Continue experiments on representative Rose Run and Black River rock powders.
- Flow through experiments on representative Rose Run and Black River sample plugs.
- Isotope, anion, cation, microscopy, and petrographic studies of compositional and textural modifications by mineral-fluid reactions.

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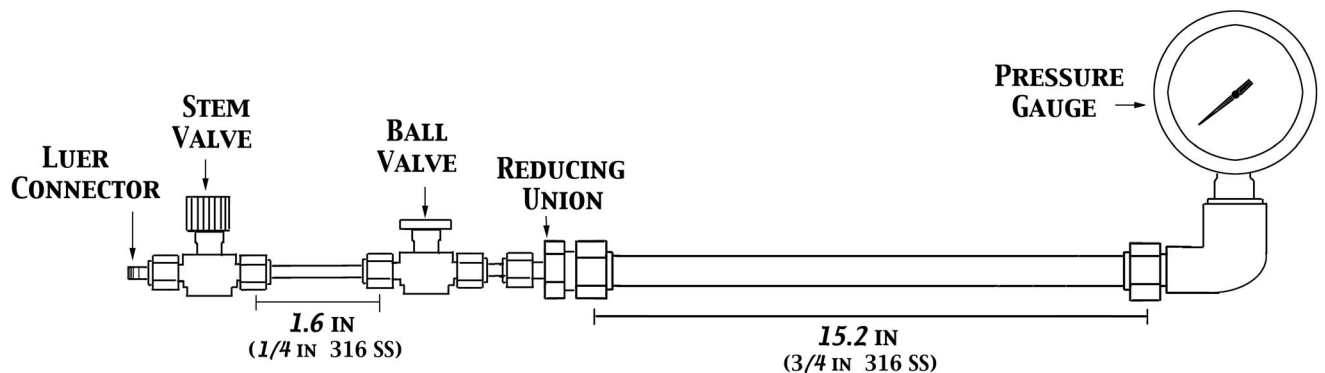
Figure 1 - Schematic diagram of the batch reactor. The main body of the reactor is 3/4 inch stainless steel tubing wrapped with heating rope (tape not shown).