Carbon Dioxide Sequestration: Effect of the Presence of Sulfur Dioxide on the Mineralogical Reactions and on the Injectivity of CO$_2$+SO$_2$ Mixtures

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This report presents experimental and modeling data on certain aspects of carbon dioxide (CO₂) sequestration. As different processes are developed and implemented to facilitate the capture of CO₂, other contaminant gases (sulfur dioxide, hydrogen sulfide and ammonia) may be present in the sequestration stream. One of the important questions is how SO₂ changes the overall chemistry of the system. It is also important to understand how this change impacts practical aspects of sequestration, such as gas injectivity. In this study, a detailed experimental investigation of the reactivity of CO₂+SO₂ mixtures with brines and rocks of specific mineralogy (typical of sequestration environments) was conducted. CO₂ with 10% SO₂ was reacted with brine and arkose at 100°C and 600 psia and the mineralogical and brine chemistry changes were compared with base-case experiments with no SO₂ in the mixture and with results of experiments carried out at low pH. The base case CO₂ experiments carried out over different time periods showed initial calcium carbonate dissolution followed by re-precipitation of calcite. A few other mineral precipitations (notably ankerite) were observed. The brine chemistry changes were consistent with the mineralogical changes observed. When SO₂ was present in the mixture, continued dissolution of calcite and precipitation of anhydrite (calcium carbonate) was observed. Numerical simulations of the injection of CO₂ and CO₂ and SO₂ mixtures into rocks of different mineralogy did not show significant differences in injectivity between the two cases. A simulation study about vertical migration and mixing was also carried out. It was shown that absolute permeabilities of the seal play an important role in free-gas and dissolved gas distribution, but relative permeability effects are also important in determining how CO₂ distributes in the saline aquifer into which it is injected.

ABSTRACT

This report presents experimental and modeling data on certain aspects of carbon dioxide (CO₂) sequestration. As different processes are developed and implemented to facilitate the capture of CO₂, other contaminant gases (sulfur dioxide, hydrogen sulfide and ammonia) may be present in the sequestration stream. One of the important questions is how SO₂ changes the overall chemistry of the system. It is also important to understand how this change impacts practical aspects of sequestration, such as gas injectivity. In this study, a detailed experimental investigation of the reactivity of CO₂+SO₂ mixtures with brines and rocks of specific mineralogy (typical of sequestration environments) was conducted. CO₂ with 10% SO₂ was reacted with brine and arkose at 100°C and 600 psia and the mineralogical and brine chemistry changes were compared with base-case experiments with no SO₂ in the mixture and with results of experiments carried out at low pH. The base case CO₂ experiments carried out over different time periods showed initial calcium carbonate dissolution followed by re-precipitation of calcite. A few other mineral precipitations (notably ankerite) were observed. The brine chemistry changes were consistent with the mineralogical changes observed. When SO₂ was present in the mixture, continued dissolution of calcite and precipitation of anhydrite (calcium carbonate) was observed. Numerical simulations of the injection of CO₂ and CO₂ and SO₂ mixtures into rocks of different mineralogy did not show significant differences in injectivity between the two cases. A simulation study about vertical migration and mixing was also carried out. It was shown that absolute permeabilities of the seal play an important role in free-gas and dissolved gas distribution, but relative permeability effects are also important in determining how CO₂ distributes in the saline aquifer into which it is injected.
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Executive Summary

Carbon dioxide (CO₂) sequestration is considered to be at least a partial solution to decrease CO₂ emissions to the atmosphere, thus stemming the rapid rise in atmospheric CO₂ concentrations. The process has been conceptualized as being able to inject large quantities of CO₂ into saline aquifers, since saline aquifers offer the most storage capacity. Mineralogical sequestration, where CO₂ gets mineralized to a carbonate or related component is the permanent storage mechanism. However, as the reactions occur, there are changes in rock properties that can impact the operation of the process. When CO₂ is being captured for sequestration, separating small amounts of other gas species from CO₂ is expensive, and if these contaminants do not have a significant impact on the sequestration process, they could be co-injected with CO₂. One such contaminant is SO₂. This project was structured into three tasks to answer the following questions.

1. How does presence of SO₂ change the base mineralogical sequestration reactions? This question was addressed by performing high-temperature, high-pressure sequestration reactions with and without presence of SO₂.

2. Does the presence of SO₂ affect the injectivity of CO₂ and SO₂ mixtures? Numerical simulations of core samples were used to understand implications of the presence of SO₂.

3. How do the seal properties affect vertical migration of CO₂? Numerical simulations of hypothetical sequestration processes were conducted to assess the impact of different domain properties on the distribution of CO₂ in the aquifer.

An experimental program was designed to study the effects of the presence of SO₂. First, baseline experiments with mixtures of CO₂, brine and rocks of specific compositions were conducted to establish reactions that take place with CO₂. A high-temperature and high-pressure reaction system was built, and reactions were carried out from temperatures ranging from 50°C to 200°C and at pressures from 600 psia to 2000 psia. All of SO₂ experiments were carried out with 10% SO₂ and 90% CO₂ mixtures. Experiments were carried out at multiple times with the identical compositions. The baseline experiments
revealed that the initial time period was dominated by dissolution of minerals like calcite. As the reactions progress, reprecipitation causes the calcium ion concentration to decrease. The presence of SO₂ changes the fundamental chemistry of the system. The calcite dissolution continues. However, precipitation of anhydrite (calcium sulfate) is observed later in time. Mineral dissolution and precipitation has implications on permanent sequestration of CO₂. These processes also affect the porosity and permeability of the system. Locally, changes in porosity and permeability can affect the injectivity of CO₂.

Simulations were performed using TOUGHREACT to assess changes in injectivities which could be caused by changes in mineralization, when SO₂ was present in the system. No systematic differences were observed in injectivity due to the presence of SO₂.

The manner in which CO₂ distributes itself in the reservoir is also important in determining the distribution of CO₂ in the gas phase and in the dissolved aqueous phase. The dissolved-phase concentration is important in determining the mineralogical reactions that occur. The vertical migration is not only governed by the absolute permeabilities of the interbedded seals but also by the relative permeabilities. In this study, a condition known as “permeability jail”, where, the relative permeabilities to both the gas and the aqueous phases remains low (close to zero) over a certain saturation range, was explored. It was shown that these types of relative permeabilities will result in seals acting as low-permeability barriers, trapping CO₂ more effectively.
Background

Carbon dioxide is the most abundant (64%) greenhouse gas (GHG). The atmospheric concentration of CO$_2$ has increased from 280 ppm during the preindustrial period to 385 ppm with about half this increase having occurred since the mid 1960s. In the United states the majority of the CO$_2$ emissions are from power plants which account for about 40% of the total emissions (IPCC 2007) and it was identified earlier by Holloway et al. (1997). Carbon dioxide sequestration appears to be an important potential method by which emissions into the atmosphere can be reduced. In this method, anthropogenic CO$_2$ is injected into geologic formations such as saline aquifers, depleted oil reservoirs (CO$_2$ enhanced oil recovery) and unmineable coal seams (enhanced coal bed methane recovery). These formations are widely available and are often in close proximity to majority of the point emission sources (Holloway et al. 1997). Injection of CO$_2$ deep underground is particularly promising because deep sedimentary formations have the potential to retain CO$_2$ in the subsurface for thousands to millions of years (Bachu 2002). In the United States, the capacity of deep saline aquifers is greater than any other geologic formation with very high estimates (Bergman and Winter 1995, 1997), and they are also found within close proximity to power plants (Bachu 1994). Aquifers with salinities exceeding 10,000 mg/l total dissolved solids are excluded by the U.S. Environmental Protection Agency as underground sources of drinking water (Xu et al. 2005). Hence these form a primary target for the eventual disposal of CO$_2$.

The temperature in these aquifers (50°-80°C) varies greatly depending on the depth and also the local geothermal gradients (Bachu 2002). Typically, CO$_2$ is injected at depths greater than 800m to ensure that it stays in the super critical state (critical temperature and pressure of CO$_2$ are 31°C and 1073 psi, respectively) (Span and Wegner 1996). The notion of CO$_2$ disposal in aquifers has been discussed in the literature with specific aquifers as target; for example, in the Netherlands (Lohuis 1993) and the Alberta Basin, Canada (Gunter 1993 Bachu 1994, Perkins and Gunter 1995, Gunter 1996, 1997 Bachu 1996).
Geologic formations, which are artificially charged with \( \text{CO}_2 \) are called carbon repositories (Kaszuba et al. 2005). Once injected \( \text{CO}_2 \) being more buoyant than water will rise until it hits an impermeable membrane or low permeability seal. This is called structural or stratigraphic trapping of \( \text{CO}_2 \). Subsequently, depending on a rate controlled by several factors such as the rate of \( \text{CO}_2 \) injection, the rate of \( \text{CO}_2 \) dissolution into the pore water, the surface area available for the reaction and the rate of diffusion of the \( \text{CO}_2 \) into the pore water away from the pore water-\( \text{CO}_2 \) interface, \( \text{CO}_2 \) dissolves in the formation water. This process is termed solubility trapping. With time \( \text{CO}_2 \) is trapped as a discontinuous phase (either in supercritical form or as dissolved \( \text{CO}_2 \)) in the pores of a formation leading to capillary trapping. \( \text{CO}_2 \) forms carbonic acid, which dissociates to form carbonate and bicarbonate ion leading to ionic trapping of \( \text{CO}_2 \). Finally these anions react with the cations resulting from the dissolution of primary minerals, due to decreased pH, which in turn leads to precipitation of carbonates permanently sequestering \( \text{CO}_2 \) (Bateman et al. 2005). Hence logically, mineral precipitation can be termed sequestration, whereas other mechanisms can be termed as storage (Kaszuba et al. 2005).

Not much importance has been given to mechanisms by which \( \text{CO}_2 \) is actually trapped as immobile mineral phases. Kaszuba et al. (2003) carried out a study to determine the extent of fluid rock interactions in addition to carbonate mineral precipitation that may occur in an experimental system that simulates geologic storage and sequestration of \( \text{CO}_2 \). They reported the precipitation of magnesite, siderite and analcime. Kaszuba et al. (2005) then carried out a study to analyze the effect of \( \text{CO}_2 \) injection on fluid rock reactions and also assess the effect of these geochemical interactions on the integrity of the cap-rock. Shale was used to model the aquitard. Such analyses for the integrity of cap-rock had been performed by Lindeberg (1997) using simple numerical models (Darcy equation and Fick’s law). They attributed the leakage of \( \text{CO}_2 \) to gravity migration with subsequent release through sub vertical fractures and faults. Few experimental studies examined geochemical reactions in a saline aquifer in response to \( \text{CO}_2 \) injection. Gunter et al. (2000) and Perkins and Gunter (1995) carried out numerical geochemical modeling studies that incorporated kinetic laws and some studies combining experiments and modeling, in which dissolution of silicate minerals in brine and precipitation of carbonate are reported. The dominant state of carbonic acid with respect to pH plays an important
role in governing the factors that leads to formation of carbonates in aquifer (Soong et al. 2002, Drever 1988, Miller et al. 2005). Miller et al. reported the formation of calcite at pressures of around 600 psi and at 150°C. Rosenbauer et al. (2005) reported the affect of presence of $SO_4^-$ on geochemical reactions and the solubilities and porosities of the repository.

**Experimental Methods**

Dirty sandstone was selected as the reacting material because of its diverse geochemical reaction basis and common occurrence in sedimentary basins (Kaszuba et al. 2005). The dirty sandstone used in our experiments is comprised of equal proportions of calcite, dolomite, quartz, microcline, andesine and chlorite. The physical properties of these materials are provided in Table 1. The minerals were crushed to 100μm and mixed to create the initial mineral assemblage. The minerals were angular to circular in shape and ranged in size from 80-100μm.

Table 1. Physical properties of the rocks used to construct the dirty sandstone.

<table>
<thead>
<tr>
<th>Rock</th>
<th>Quartz</th>
<th>Andesine</th>
<th>Dolomite</th>
<th>Chlorite</th>
<th>Microcline</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>SiO₂</td>
<td>Na₃Ca₃Al₂Si₄O₁₀</td>
<td>CaMg(CO₃)₂</td>
<td>(Fe, Mg, Al)₄(Si, Al)₈O₁₀(OH)₈</td>
<td>KAlSi₃O₈</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Class</td>
<td>Silicates</td>
<td>Silicates</td>
<td>Carbonates</td>
<td>Silicates</td>
<td>Silicates</td>
<td>Carbonates</td>
</tr>
</tbody>
</table>

The experimental apparatus is illustrated in Figure 1. It consists of series of four stainless steel reactors made of 316-grade stainless steel, which were rated for 4000 psi at 600°C. The reactors were pressure sealed with high-pressure SWAGELOK fittings. The reactor has the provision for retrieving the rock sample without disturbing it through a detachable cap (Swagelok fitting) at the bottom. The CO₂ was pressurized in the reactor using a single cylinder high pressure positive displacement pump. The flow of CO₂ into the reactor was controlled using high-pressure needle valves. Dry CO₂ (drawn from a CO₂ cylinder equipped with a siphon) was used in all the experiments. High-purity nitrogen was used to pressure test the entire setup at 3000 psi. The temperature was controlled
using a bench top temperature controller with SPECVIEW as the interface via K-type thermocouples. Brine was prepared from laboratory grade NaCl with the initial composition shown in Table 2.

<table>
<thead>
<tr>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Ba</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>μg/L</td>
<td>μg/L</td>
<td>μg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
</tr>
<tr>
<td>23032</td>
<td>1</td>
<td>&lt;6</td>
<td>&lt;4</td>
<td>&lt;8</td>
<td>&lt;1</td>
<td>54</td>
<td>&lt;2</td>
<td>0.4</td>
<td>&lt;6</td>
<td>26542</td>
</tr>
</tbody>
</table>

High purity nano-filtered de-ionized (DI) water was used to prepare the brine samples. Injection of approximately 7cc of CO₂ into the reactor increases the pressure of the experimental system to 2200 psi. Subsequently the pressure decreased to 2000 psi over a period of 37 hrs. The total pressure of the experimental system stabilized around 2000 psi for the duration of the experiment with the exception of a few fluctuations, which can be attributed to changes in the ambient temperature in the laboratory. Three sets of experiments were carried out at different conditions with different feed gas compositions. Table 3 lists the conditions adopted for each of these experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>Pressure (psi)</th>
<th>Gas Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A</td>
<td>200</td>
<td>2000</td>
<td>CO₂</td>
</tr>
<tr>
<td>Set B</td>
<td>100</td>
<td>2000</td>
<td>CO₂</td>
</tr>
<tr>
<td>Set C</td>
<td>100</td>
<td>600</td>
<td>90%CO₂+10%SO₂</td>
</tr>
<tr>
<td>Set D</td>
<td>100</td>
<td>2000</td>
<td>CO₂ with an initial pH of 3</td>
</tr>
</tbody>
</table>

The advantage of using such apparatus over the previous experimental setup described in Seyfried et al. (1987), which was adopted by Kaszuba et al. (2003, 2005) and Rosenbauer et al. (2005), is that we can correlate the changes in mineralogy with the changes in brine chemistry at each stage the sample is collected. This provides a comprehensive picture of the geochemical interactions taking place. Sampling does not disturb the system, and mineralogical changes can be viewed in light of the changes in brine chemistry. The rock
analysis was carried out using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses.

The initial sample was prepared by mixing equal proportions of rock (0.5 grams each). After the experiment the sample was retrieved from the reactor by detaching the bottom (wherein the sample rests in a cap) and carefully removing the sample without disturbing the crystals (of the minerals) that might have grown (precipitated) on the surface. The sample was dried overnight at 60°C, a temperature not high enough to alter the crystal structure of any minerals. The sample is then retrieved, cooled and split into equal fractions for XRD and SEM/EDS analyses. After the experiments the brine samples were diluted and filtered using Whatman 40 filter paper (retention capacity of 8μm) under a vacuum. The sample was then divided into sub equal fractions for cation and anion analyses. The sample was acidified with addition of sulfuric acid to prevent any precipitation. The dissolved cations were analyzed using ICPMS and dissolved anions by ion chromatography.

Figure 1. Schematic diagram of the experimental setup.
Results

Initial examination of the rock surface

SEM and XRD analyses were performed on the rock samples. The SEM analysis was done using a HITACHI SEM equipped with an EDS analyzer. The EDS analyses identified the clay minerals, mainly plagioclase feldspar (Figure 2a) and illite (minor quantities) (Figure 2b) and chlorite to be the major silicate minerals and calcite and dolomite as the carbonate minerals in the starting material. The SEM analysis was performed at different resolutions to measure the exact chemical composition of the mixture and to ensure uniform composition.

Figure 3 shows the XRD analyses for two initial rock samples and indicates the overlap of the spectra for two initial samples, which turn out to be identical. This was done to ensure homogeneity during mixing of the six different rock samples to form the initial mineral assemblage. The initial sample XRD analysis shows the peaks of the minerals used to prepare the sample. These peaks serve as a reference for the analysis of the reacted sample.

Figure 2a: SEM image of the host rock at 1kx magnification showing plagioclase feldspar deposits on quartz
Figure 2b: SEM image of the host rock at 1kx magnification showing branched aggregates of plagioclase feldspar and minor quantities of illite

Figure 3: Initial XRD analyses of the host rock

**Experimental set A (200°C and 2000 psi)**

The experimental conditions were similar to that of Kaszuba et al. (2003 and 2005). Under these conditions the rates of silicate dissolution are accelerated. However the aqueous solubility of CO$_2$ is generally lower at elevated temperatures and salinity and
greater at elevated pressure. Using SUPCRT92 the maximum dissociation for carbonic acid dissolution occurs at 50°C, above which log K decreases continuously with increasing temperature as a result of which initially weak acid becomes increasingly weaker at elevated temperatures (Rosenbauer et al. 2005). Consequently these experiments at ~200°C were carried out for a relatively longer time period (123 days) to see detectable changes in the host rock. For the reacted time period, pronounced changes were observed in the starting material. The major change in composition is observed in andesine, chlorite and quartz. While andesine and dolomite were observed to dissolve into the brine, calcite, quartz and chlorite were found to precipitate. The precipitation of quartz was not conclusive since the change in its composition was within the uncertainty in measurement with XRD. This XRD analyses gives a preliminary picture of the changes occurring in mineral phases and a preview of what to expect in the SEM/EDS analyses. To study the surface chemistry and to identify the precipitation or dissolution patterns of the dominant minerals on the samples the initial and the reacted samples were analyzed using SEM. The sample is mounted on a carbon tape and is gold coated in an inert (argon) environment to charge the surface. SEM analysis requires careful observation of the surface of the sample at a very high resolution. The portions of the surface, which indicate the deposition of calcite as layers or crystals, are usually picked for analysis.

Table 4: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial (wt%)</th>
<th>Reacted (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>23.9</td>
<td>18.28</td>
</tr>
<tr>
<td>Calcite</td>
<td>19.1</td>
<td>22.4</td>
</tr>
<tr>
<td>Dolomite</td>
<td>17.4</td>
<td>14.65</td>
</tr>
<tr>
<td>Quartz</td>
<td>15.7</td>
<td>17.8</td>
</tr>
<tr>
<td>Chlorite</td>
<td>14.4</td>
<td>17.92</td>
</tr>
<tr>
<td>Microcline</td>
<td>9.4</td>
<td>8.96</td>
</tr>
</tbody>
</table>

Calcium carbonate was observed to grow on the sample as layers (Figure 5a, 5b). Due to the increased acidity caused by the formation of carbonic acid, the primary minerals such
as dolomite and calcite undergo dissolution. The calcium cation should be from dolomite or calcite, because the XRD analyses reveal the dissolution of these minerals. The calcium ion thus liberated into the solution forms calcite by combining with the carbonate ion from the acid consuming one mole of CO₂ in the process. Calcium carbonate deposition is a clear indication of the consumption of CO₂ in this reaction. Chunks of halite were seen deposited on the reacted surface (Figure 5c). Halite must be from the brine used in the experiment because the sample was dried overnight at 60°C before the analysis.

Ankerite, (iron carbonate) was seen growing as aggregates on the reacted surface usually intergrown with the initial minerals (usually quartz) (Figure 5d). The source of iron for ankerite was the dissolution of chlorite, a magnesium rich clay in the initial sample. The XRD analyses, which shows the dissolution of chlorite, confirms this. The qualitative X-ray analysis by EDS confirmed the identification of ankerite and it was absent in the initial mineral assemblage at the start of the experiment. The growth was seen as aggregated units in the interstitial spaces between the primary minerals especially quartz.

Figure 4: XRD overlap of the initial and the reacted samples for the experiment at 200 C and 2000 psi. The distinctive peaks seen are halite and chlorite and calcite
Figure 5a: SEM image at 6kx magnification showing growth of calcite as layers

Figure 5b: SEM image at 12kx magnification showing precipitation of calcite aggregates on quartz
Figure 5c: SEM image at 3kx magnification showing deposition of Halite chunks

Figure 5d: SEM image of Ankerite growth in the final sample
**Experimental set B**

The experiments were carried out with the same experimental setup used for the Set A experiments with CO$_2$ as feed gas and with the same rock composition at 100°C and 2000 psi. As mentioned earlier this experimental setup provides the luxury of analyzing the rock and the brine chemistry at the same time, which enables identification of changes in the rock chemistry and the changes in the concentrations of the corresponding ions in the brine chemistry. The samples were collected from the reactor after 62 days and were heated at 60°C overnight and prepared for analysis on both SEM and XRD.

Table 5 shows the changes in rock chemistry as identified by the XRD analysis. The quantitative estimates of the minerals before and after the experiments were obtained by XRD. Since small amounts of precipitates formed, attempts to quantify produced solids proved difficult. Hence the changes in the initial mineral assemblage and the mineral assembly after the reaction were calculated. These changes can be corroborated with the precipitated minerals seen in the SEM/EDS analysis, and a reaction mechanism leading to the precipitation of new minerals can therefore be postulated. In the analysis all the participating minerals (constituents of arkose or dirty sand) participate in the reaction. The major change is seen in the composition of dolomite and feldspars (microcline and andesine) with a small change in calcite and chlorite. The change in quartz composition was not expected and dissolution of quartz usually doesn’t occur at pH 5. But as the pH increases and hits a pH of about 7 the H$_4$SiO$_4$ dissociates leading to the dissociation of silica (Dreever 1988).

Table 5: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial (wt%)</th>
<th>Reacted (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>25.1</td>
<td>29.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>Dolomite</td>
<td>14.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>22.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Chlorite</td>
<td>8.2</td>
<td>9</td>
</tr>
<tr>
<td>Microcline</td>
<td>15.2</td>
<td>16.2</td>
</tr>
</tbody>
</table>
Table 6 shows the XRD analysis of the mineral assemblage after 134 days. While dissolution patterns dominate the XRD analysis in the sample after 62 days precipitation patterns dominate after 134 days. Andesine, calcite and microcline are found precipitating while dolomite and quartz composition decreased in the final experiment. The reason for the decrease in quartz can be attributed to the same reasoning as given for the 62 days experiment. These results are in good correlation with the brine chemistry analysis and also the SEM/EDS analysis for the rock explained in the sections to follow.

Table 6: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis after 134 days.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial (wt%)</th>
<th>Reacted (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>25</td>
<td>30.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>15</td>
<td>19.8</td>
</tr>
<tr>
<td>Dolomite</td>
<td>14.8</td>
<td>11</td>
</tr>
<tr>
<td>Quartz</td>
<td>22</td>
<td>14.8</td>
</tr>
<tr>
<td>Chlorite</td>
<td>7</td>
<td>7.2</td>
</tr>
<tr>
<td>Microcline</td>
<td>15</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Figures 6 (6a 6b 6c) show the SEM analysis of the initial sample, sample after 62 days and 134 days, respectively. The calcite in the initial samples serves as a standard to examine the precipitation and the dissolution patterns in the samples at different stages of the experiments. The precipitate from the experiment for 134 days was chosen because it was a reaction in which calcite precipitated as determined by the XRD. Figure 8b shows the pronounced dissolution patterns in the sample after 62 days. Dissolution occurs mainly by the formation of few deep etch pits and some shallow ones, almost at the same position in the initial dissolution of the surface. Dissolution occurs quickly which is followed by precipitation as seen in the Figure 6c (experiment carried out for 134 days). These layers and crystals of calcite are seen growing as amorphous mass intergrown with the starting minerals. These calcite crystals (Figure 7a) are highly irregular in shape and show no consistency in size. One calcite crystal had a width of about 10μm and most of the particles appear much smaller than this size. Hence it can be concluded that not all
precipitates were collected when the brine was filtered (with a filter paper of 8 μm retention capacity). Figure 6d shows deposition of a new-phase analcime or kaolinite on the reacted surface.

Kaolinite was not identified in the XRD analyses because it shares the same primary peak with one of the minerals in the initial assemblage, chlorite. However, it was identified in the reacted assemblage. The growth was seen as aggregated units in the interstitial spaces between the primary minerals, especially quartz.

Figure 6a: SEM image showing calcite in the initial samples
Figure 6b: SEM image showing calcite in the sample showing dissolution after 62 days.

Figure 6c: SEM image showing the growth of calcite after 134 days indicative of mineral precipitation reactions.
Figure 6d: SEM image showing the growth of new phase probably analcime on the surface

Figure 7a: Calcite crystals growing in interstitial spaces between plagioclase feldspar
Figure 7b: Kaolinite deposition on quartz

Figure 8: EDS analysis confirming the presence of ankerite in the reacted sample
**Brine chemistry during the reactions**

The analysis of the changes in the concentrations of the principal ions in the brine during the experiment helps provide a clear understanding of the interactions between the rock and dissolved CO$_2$ at the brine-mineral interface (Figure 9). Injection of supercritical CO$_2$ caused significant changes in the brine chemistry. These changes are more evident when compared with the changes in the rock chemistry. The Na ion concentration increased by approximately 17% after 14 days of injection, continued to increase for 62 days (by about 47%) and continued to decrease for the rest of the experiment. The Na concentration prior to the termination of the experiment was 16% less the initial concentration of Na. The Cl concentration followed a similar trend. It increased by approximately 19% at the end of 14 days after injection and increased for 62 days. It then continued to decrease for the rest of the experiment with the final concentration being 5% less than the initial concentration. The pH of the system decreased to approximately 4.5 at the end of 27 days and then stabilized at around 6.7 for the rest of the experiment. All the pH measurements as well as the ion concentrations were calculated by depressurizing the reactors to atmospheric conditions after the experiments. The pH calculated using the Geo-chemists’ workbench for this system stabilized around 7.09.

The changes in the concentrations of the principal ions did not follow a particular trend like that of Na and Cl concentrations. The Ca ion concentration increased by about 90% after 14 days and continued to increase for 42 days after, when it decreased with the final concentration approximately 47% less than the highest concentration measured. The K ion concentration exhibited a similar trend to that of Ca ion with the concentration increasing abruptly and continuing to increase until 62 days after which it decreased. The increase in the Ca ion concentration can be attributed to the dissolution of the primary carbonate minerals calcite and dolomite liberating Ca ion into the brine. The K ion concentration increase was due to the dissolution of the microcline, which is potassium feldspar, and the silicate dissolution reactions are the fastest in a low pH geochemical system. The Mg ion concentration increased by approximately 52% by 27 days and continued to increase until 62 days, after which it decreased with the final concentration 42% lower than the initial concentration measured at 27 days. This increase was mainly
due to the dissolution of dolomite and chlorite. Iron (Fe) concentration decreased throughout the experiment, and the final concentration was approximately 27% lower than the initial concentration. The decrease in the concentrations of the Ca, Mg and K ions by 47%, 42% and 27%, respectively, in the latter stages of the experiment are an indication of new minerals with the primary composition of these ions precipitating in the solid phase. The Si concentration followed a very unique trend. It increased by 14% after 27 days then decreased slightly (2%) and then increased by about 32% until the termination of the experiment. Because the increase of 2% was within the experimental and analytical uncertainty, the concentration can be considered stable from 27 days to 42 days. The Si concentration increase can be attributed to the dissolution of feldspars, microcline and andesine, which are the most sensitive minerals to decreasing pH (Dreever 1988). Hence the silicate dissolution dominates the geochemical reactions in the system. This also is evident from the silica coating on all the samples analyzed in the SEM with a distinctive Si peak in the EDS analyses. This is due to the deposition of Si from the brine on to the rock when the solid sample is dried prior to the analysis.
Figure 9: Changes in concentrations of the principal ions during the experiment

Figure 10 is the best example of the changes in the brine chemistry corroborated with the alterations in the solid phase. The changes occurring in the brine reflect in the rock chemistry too. The samples collected at the end of 62 days and 134 days were selected to represent these changes, and Ca ion was chosen as the principal ion undergoing the change. At the end of 62 days and also through the first 62 days, the Ca ion concentration increased in the brine indicating the dissolution of primary carbonate minerals calcite and dolomite in the brine. It is also clearly seen in the SEM analysis of the rock sample collected at the end of 62 days where calcite dissolution pattern dominates. From 62 days through 134 days, the Ca ion concentration decreases, which implies that Ca bearing minerals should precipitate in the solid phase. This is also evident from the SEM analysis of the sample collected at the end of 134 days where layers and crystals of calcite are seen growing as amorphous mass intergrown with the starting minerals (especially quartz).
Experiment Set C

The experimental setup used for the CO₂ experiments was used for these sets of experiments. The temperature was 100°C, and pressure was 600 psi. The initial brine composition was the same. The composition of the mineral assemblage was also the same. The only change is in the feed gas composition which is 10% SO₂ with 90% CO₂. The gas is a calibrated mixture provided by AIRGAS in cylinders with a maximum deliverable pressure of 600 psi. There were two reactors running under identical conditions. The rock was equilibrated with brine for a period of 36 days, and then the gas was injected into the system. The first reactor was brought down after 14 days and the second after 37 days.

XRD analyses of the sample show pronounced changes in the rock chemistry. The initial XRD patterns show an almost uniform distribution of the primary minerals in the host
rock. For the initial sample i.e., the experiment carried out for 14 days, there is a large dissolution of calcite and dolomite with dissolution of other silicate minerals (plagioclase feldspars and microcline), and also dissolution of the mineral chlorite (Table 7). The XRD pattern also shows the precipitation of hydrated calcium sulfate, bassanite and some anhydrite, but they were dominated by the pronounced dissolution patterns of the primary minerals calcite, dolomite and chlorite.

Table 7: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis after 14 days.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial (wt%)</th>
<th>Reacted (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>Calcite</td>
<td>17.6</td>
<td>4</td>
</tr>
<tr>
<td>Dolomite</td>
<td>12.1</td>
<td>8</td>
</tr>
<tr>
<td>Quartz</td>
<td>18.8</td>
<td>15</td>
</tr>
<tr>
<td>Chlorite</td>
<td>16</td>
<td>13.9</td>
</tr>
<tr>
<td>Microcline</td>
<td>18</td>
<td>14</td>
</tr>
</tbody>
</table>

For the experiment, which was terminated after 37 days, the XRD pattern shows continued dissolution of calcite, a slight increase in dolomite and the precipitation of bassanite, anhydrite and minute quantities of kaolin (Table 8). Concluding of kaolin deposition in the sample is very difficult because kaolin shares primary peaks with chlorite, which was a part of the initial mineral assemblage. Consequently when a qualitative EDS analysis on the sample was run with the SEM, kaolin was detected which bolstered the finding in the XRD.

Table 8: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis after 37 days.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial (wt%)</th>
<th>Reacted (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>Calcite</td>
<td>17</td>
<td>2</td>
</tr>
<tr>
<td>Dolomite</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Quartz</td>
<td>19</td>
<td>23.7</td>
</tr>
<tr>
<td>Chlorite</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>Microcline</td>
<td>18</td>
<td>23.7</td>
</tr>
</tbody>
</table>
The SEM analyses of the host rock after the experiment showed pronounced dissolution of all the primary minerals involved in the reaction. The product also had widespread deposition of anhydrite crystals. These crystals were usually distinct and were seen growing either on the surface of quartz or in the interstitial spaces between the host rock (especially feldspars anorthite and microcline). The final pH of the system in the two separate experiments was 1.9 after 14 days and 2.48 after 37 days.

Anhydrite occurs as large discrete bladed crystals on the surface of the host mineral especially on anorthite, which is plagioclase feldspar. The crystals were visible at 2k× resolution usually 6-8μm wide. The crystal faces of anorthite were pitted and rough. EDS analysis confirmed the presence of anhydrite, which was absent in the initial mineral assemblage. Hence the precipitation of anhydrite can be explained by the increased acidity following the injection of the gas mixture. Primary minerals calcite and dolomite underwent dissolution, and this led to secondary precipitation of anhydrite. The crystalline masses of anhydrite are possibly due to acidity in the brine and the presence of the supercritical CO₂ phase, which lead to rapid crystal nucleation and growth. Chunks of silica were seen deposited on these anhydrite crystals (Figure 14a). The increased acidity led to rapid dissolution of silicate bearing phases i.e., plagioclase and potassium feldspar, which led to the release of silica into the brine. When the sample was prepared for analysis (dried overnight), the silica deposited on the surface and the EDS analysis supports this mechanism. The silica chunks are 2-10μm in cross section.

There were pronounced dissolution patterns for most of the primary minerals involved in addition to the precipitation of anhydrite. The calcite chunk in the figure shows the dissolution of calcite, which is also evident from the increase in the calcium ion concentration in the brine, which is discussed later. The alteration of the silicate phases occurs as the dissolution of primary feldspars, the plagioclase feldspar and also the potassium feldspar (microcline). Such dissolution patterns were ubiquitous in addition to the precipitated anhydrite crystals. All the mineral surfaces were rough and pitted, which are the most commonly observed dissolution patterns.

There were other minerals, which were found as traces in the XRD analysis, but their presence was confirmed in the subsequent EDS analysis. Kaolinite was observed growing
the interstitial spaces of the host rock (mainly plagioclase feldspar). It was seen growing as hollow crystals (Figure 16), which is the typical manner in which we see crystalline feldspars growing as reported by Moore et al. (2005) in their characterization of natural carbonate reservoirs in Colorado plateau. Figure 18a shows one face of the kaolin crystal growing. From the sample collected after 14 days the dissolution patterns dominated with only traces of new mineral precipitation whereas after 37 days there was more prominent precipitation and obvious dissolution.

![XRD analysis of the reacted sample](image)

Figure 11: XRD analysis of the reacted sample
Figure 12a and 12b: Growth of anhydrite crystals after 37 days
Figure 13: EDS analysis confirming the growth of anhydrite on anorthite and quartz

Figure 14a: Anhydrite crystal with some deposits of silica
Figure 14b: Growth of discrete anhydrite crystal

Figure 15: pronounced dissolution patterns of calcite after 14 days
Changes in brine chemistry in Set C

The presence of SO$_2$ in the feed gas stream along with CO$_2$ alters the brine chemistry to a great extent (Figure 17). The Na ion concentration increased for 14 days by about 8% and decreased for the remainder of the experiment. Prior to the termination of experiment there is a 6% decrease when compared to the initial concentration. The Cl concentration decreased by about 11% before increasing in the latter part of the experiment. The principal ion Ca increased throughout the experiment with a final increase of almost 80%, which indicates excessive dissolution of calcite and dolomite in the system. This increase is almost 1.5 times greater than the increase observed in experiments with CO$_2$ as pure gas. The Mg ion concentration decreased by about 18% in the final sample collected, which varies to a great extent from the earlier experiment because Mg was found to increase at the same time in that experiment. The decrease in Mg ion is less than the increase in Ca ion, which implies that Mg ion is precipitating in another phase than dolomite. This might be due to two reasons. The first being the dissolution of calcite or dolomite and the second being the dolomotization of calcite. The slight decrease in magnesium ion concentration leads us to conclude that the latter may be dominant. The dissolution of calcite and dolomite was evident in the XRD analyses. In the experiment
the abrupt increase in Ca ion from the dissolution of primary carbonate minerals, calcite and dolomite, causes the SO$_4$ to precipitate as anhydrite, gypsum or bassanite (hydrated CaSO$_4$). The Al ion concentration decreased by about 1% and decreased rapidly with a slight rise in the latter stages of the experiment. This trend was similar to that observed in the earlier experiment but the decrease was much steeper in this case. The Fe concentration followed a similar trend decreasing throughout. The K ion increased abruptly because of the feldspar dissolution reactions then decreased probably due to kaolin precipitation as observed in the SEM analysis.

![Figure 17: changes in the brine chemistry of principal ions during the experiment](image-url)
### Table 9: Brine composition in set C

<table>
<thead>
<tr>
<th>Time</th>
<th>Na (mg/l)</th>
<th>Mg (mg/l)</th>
<th>K (mg/l)</th>
<th>Al (µg/l)</th>
<th>Fe (µg/l)</th>
<th>Ca (mg/l)</th>
<th>Si (mg/l)</th>
<th>S (mg/l)</th>
<th>Cl (mg/l)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>11376</td>
<td>587</td>
<td>17</td>
<td>43</td>
<td>27</td>
<td>11</td>
<td>&lt;1</td>
<td>296</td>
<td>38852</td>
</tr>
<tr>
<td>14</td>
<td>12137</td>
<td>569</td>
<td>26</td>
<td>39</td>
<td>27</td>
<td>14</td>
<td>1.5</td>
<td>370</td>
<td>38742</td>
</tr>
<tr>
<td>21</td>
<td>10754</td>
<td>461</td>
<td>72</td>
<td>1</td>
<td>21</td>
<td>176</td>
<td>21.6</td>
<td>590</td>
<td>34629</td>
</tr>
<tr>
<td>37</td>
<td>10599</td>
<td>368</td>
<td>64</td>
<td>4</td>
<td>19</td>
<td>994</td>
<td>34.8</td>
<td>1551</td>
<td>37157</td>
</tr>
</tbody>
</table>

### Experiment set D

![XRD analysis of the reacted sample](image)

Figure 18: XRD analysis of the reacted sample
Table 10: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis after 21 days

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial</th>
<th>Reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>25.1</td>
<td>29.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>15</td>
<td>19.1</td>
</tr>
<tr>
<td>Dolomite</td>
<td>14.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>22.2</td>
<td>15.6</td>
</tr>
<tr>
<td>Chlorite</td>
<td>8.2</td>
<td>9</td>
</tr>
<tr>
<td>Microcline</td>
<td>15.2</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table 11: Quantitative estimates of changes in compositions of the minerals (wt%) before and after the experiment from XRD analysis after 37 days

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial</th>
<th>Reacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andesine</td>
<td>25.1</td>
<td>24.5</td>
</tr>
<tr>
<td>Calcite</td>
<td>15</td>
<td>11.1</td>
</tr>
<tr>
<td>Dolomite</td>
<td>14.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>22.2</td>
<td>21.6</td>
</tr>
<tr>
<td>Chlorite</td>
<td>8.2</td>
<td>9</td>
</tr>
<tr>
<td>Microcline</td>
<td>15.2</td>
<td>14.6</td>
</tr>
</tbody>
</table>

These experiments were performed at an initial pH of 3 by acidifying the brine with 0.1 ml of 1M sulfuric acid. The experiments were carried out at 100°C and 2000 psi for 14, 21 and 37 days respectively. The XRD analyses in Tables 10 and 11 show dissolution of the primary minerals, calcite and dolomite, and precipitation of other constituents. However precipitation of minerals was not observed in the SEM analyses. The dissolution patterns of calcite and dolomite dominate the reacted rock. Brine chemistry also supports this (Figure 20). The concentrations of the principal ions increase indicating that the carbonate minerals are undergoing dissolution during the course of the experiment.
Figure 19a: pronounced dissolution patterns of calcite after 21 days

Figure 19b: pronounced dissolution patterns of calcite after 37 days
Figure 20: changes in the brine chemistry of principal ions during the experiment

**Study of the vertical movement of the CO₂ plume**

Vertical migration of CO₂ in the formation into which it is injected is an important phenomenon. CO₂, being lighter than water, overrides the water and reaches the top of the formation. On a macro-scale, it is important to capture such a buoyancy-driven transport, since it affects all aspects of CO₂ trapping. The dissolution of CO₂ at the interface, creating a heavier fluid and causing density-driven instabilities has been studied. The gravity fingers created can range in scale from one millimeter to several meters. This particular component of the process embodies all of the elements of the parent sequestration process in the sense that equilibration does not occur over
engineering time scales, and several spatial scales govern how the dissolution and equilibration proceeds.

In this task we studied the vertical migration of CO$_2$ in the aquifer and the parameters that control the migration and subsequent distribution of CO$_2$ in the various phases.

All of the simulations were performed using TOUGHREACT. The domain used in the simulations is shown in Figure 21, and the general conditions of simulations are summarized in Table 12.

![Figure 21: The domain used to study the vertical migration and distribution of CO$_2$.](image)

Figure 21: The domain used to study the vertical migration and distribution of CO$_2$. 
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>1<em>60</em>60</td>
</tr>
<tr>
<td>Grid block size</td>
<td>100ft<em>10ft</em>10ft</td>
</tr>
<tr>
<td>Model size</td>
<td>100ft<em>600ft</em>600ft</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.30 (0.15 for seal)</td>
</tr>
<tr>
<td>Permeability (matrix)</td>
<td>100md</td>
</tr>
<tr>
<td>Permeability (seal)</td>
<td>1~100md</td>
</tr>
<tr>
<td>Temperature</td>
<td>75°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>200bar</td>
</tr>
<tr>
<td>Salinity</td>
<td>3-6.0wt%</td>
</tr>
<tr>
<td>Injection rate</td>
<td>2.3177*10^3kg/hr</td>
</tr>
<tr>
<td>Injection period</td>
<td>258.4 days</td>
</tr>
</tbody>
</table>

In addition to studying the sensitivity of parameters to the absolute permeability of the seal and the formation, additional simulations were performed with relative permeabilities where both the phases are essentially immobile (a situation that is termed “permeability jail” in some other gas flow applications). The relative permeabilities for the situation with permeability jail are shown in Figure 22.
Distributions of free and dissolved CO$_2$ concentrations are shown in Figure 23. In the uniform permeability case, the free-CO$_2$ concentration is highest at the top of the formation. If the top of the formation is breached, the CO$_2$ will leak outside of the target zone. If permeability-jail type relative permeabilities are used in the seal, the seal becomes an effective trapping layer, and CO$_2$ is better distributed in the aqueous phase as well.
When the permeability of the seal is reduced to 1 md, the vertical migration of CO₂ predominantly occurs through the holes in the low permeability seal, and the permeability jail-type relative permeabilities do not change the distributions of the free and dissolved CO₂ concentrations significantly (Figure 24).
Free CO₂: k=1 md, low permeability

dissolved CO₂: k=1 md, low permeability

Free CO₂: k=1 md, permeability jail

dissolved CO₂: k=1 md, permeability jail

Figure 24: Vertical distribution of CO₂ (as free gas phase, and in the dissolved state) for the domain with uniform permeabilities and in the system with “permeability-jail” relative permeabilities in the seal. The seal permeability is 1 md in all the simulations.
Numerical simulation flow experiments

For all simulation experiments, the TOUGHREACT simulator was utilized (Xu et al., 2006), which includes full thermal-hydrologic-chemical coupling – multiphase CO₂ flow, heat flow, and reactive transport. TOUGHREACT has a large user community and is widely used for predicting reactive transport and trapping behavior of injected CO₂ in storage reservoirs (Xu et al. 2003, 2004, 2005, 2006, 2007; Audigane et al. 2007, Gherardi et al. 2007, and Zhang et al. 2009). TOUGHREACT utilizes the finite volume method (FVM) to solve the multiphase groundwater flow equation and uses a generalized form of Darcy’s Law to evaluate flow velocities. Because all flow experiments and simulations involve brine, a robust chemical model of brine- CO₂-SO₂ interactions was needed. The original TOUGHREACT code (Xu et al., 2006) computed activity coefficients of charged aqueous species using an extended Debye-Huckel (DH) equation. The DH model can deal with ionic strengths from dilute to moderately saline water. During the course of the Yucca Mountain project, a Pitzer ion-interaction model was implemented into TOUGHREACT (Zhang et al., 2008) using the model formulated by Harvie et al., (1984).

For additional details about the TOUGHREACT simulator, the reader is referred to many recent sequestration publications (e.g., Xu et al. 2007; Audigane et al. 2007, Gherardi et al. 2007, Zhang et al. 2009).

The simulation work consisted of core-scale simulations of laboratory experiments. The core-scale simulations of the laboratory flow tests were assembled to evaluate the results of the tests, including explicit processes of reactive transport with chemical diagenesis and associated porosity and permeability changes. Results and parameters from these calibrated simulations were used to interpret potential effects on injectivity evolution and seal integrity. Mechanical deformation was not included in this first generation of experiments and associated simulations. Ultimately, these data and results will be used to aid injectivity design of future pilot-scale and commercial-scale sequestration tests, with goals of minimizing risks and maximizing injectivity.

The processes and parameters that were investigated using the models included:
- Core-scale simulations to replicate each lab experiment and calibrate models

- Simulated/calibrated evolution of:
  - matrix lithology (diagenetic)
  - porosity
  - permeability
  - chemical top-seal degradation
  - evolution of reservoir (sequestration target) hydrologic properties
  - other parameters/processes, as appropriate

The San Juan Basin of northern New Mexico was selected for this research because it is the site of a pilot-demonstration of CO₂ injection under the auspices of the Southwest Regional Partnership on Carbon Sequestration (SWP), a consortium sponsored by NETL. The SWP is in its sixth year, and currently deploying multiple injection tests throughout the region. Because of SO₂’s and its potential for degrading CO₂-injectivity, it is important to do this test.

San Juan Basin rock core samples were acquired for laboratory testing. The subject formations for deep saline sequestration testing are the Jurassic-aged Entrada sandstone and the Mississippian-aged Leadville limestone. The core samples were

Figure 25. Photographs of San Juan basin core taken from the Carson Federal G #1 well
analyzed for fractures and other heterogeneities. Results of these analyses indicate that these formations possess many minor chemical constituents, and our initial simulations of these specific rocks suggest that interpretation of reactive-transport results will be complicated by these minor constituents. Thus, to maximize applicability (transferability/portability) of our results to other studies, we elected to focus on pure end-member archetypes of these formations represented by the Indiana Limestone and the Berea Sandstone. In the last few months of this project, we acquired Indiana and Berea core from Fisher Scientific company and repeated mineralogic and hydrologic (porosity and permeability) analyses of the core (Table 12).

Table 13: Berea and Indiana formation cores subject to final laboratory testing and flow simulation analyses.

<table>
<thead>
<tr>
<th>Core Lithology</th>
<th>Formation</th>
<th>Permeability (mD)</th>
<th>Porosity (%)</th>
<th>UCS (psi)</th>
<th>Length (in)</th>
<th>Diameter (in)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea Sandstone</td>
<td>Kipton</td>
<td>60 – 100</td>
<td>18 - 20</td>
<td>6000 -8000</td>
<td>24</td>
<td>2</td>
</tr>
<tr>
<td>Indiana Limestone</td>
<td>Bedford</td>
<td>2 – 4</td>
<td>10-12</td>
<td>4500</td>
<td>24</td>
<td>2</td>
</tr>
</tbody>
</table>

**Reactive transport simulations**

*CO₂-brine with SO₂ flow:* Core simulations of NaCl- CO₂ with SO₂ were conducted and results compared to the CO₂-brine. Injected CO₂-brine in these tests included 1.45 x 10⁻⁶ M SO₂. In both experimental and simulated flow tests, we observed no appreciable effects on porosity, permeability, and therefore injectivity. The simulation results were extended to 10 years, but did not exceed a decade and we did not increase SO₂ concentrations in these simulations.
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**Figure 2b:** SEM image of the host rock at 1kx magnification showing branched aggregates of plagioclase feldspar and minor quantities of illite

**Figure 3:** Initial XRD analyses of the host rock.

**Figure 4:** XRD overlap of the initial and the reacted samples for the experiment at 200 C and 2000 psi. The distinctive peaks seen are Halite and Chlorite and Calcite
Figure 5a: SEM image at 6kx magnification showing growth of calcite as layers

Figure 5b: SEM image at 12kx magnification showing precipitation of calcite aggregates on quartz

Figure 5c: SEM image at 3kx magnification showing deposition of Halite chunks

Figure 5d: SEM image of Ankerite growth in the final sample

Figure 6a: SEM image showing Calcite in the initial samples

Figure 6b: SEM image showing calcite in the sample showing dissolution after 62 days

Figure 6c: SEM image showing the growth of Calcite after 134 days indicative of mineral precipitation reactions.

Figure 6d: SEM image showing the growth of growth of new phase probably analcime on the surface

Figure 7a: Calcite crystals growing in interstitial spaces between plagioclase feldspar

Figure 7b: Kaolinite deposition on quartz

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Figure 11: XRD analysis of the reacted sample

Figure 12a and 12b: Growth of anhydrite crystals after 37 days

Figure 13: EDS analysis confirming the growth of anhydrite on anorthite and quartz

Figure 14a: Anhydrite crystal with some deposits of silica

Figure 14b: Growth of discrete anhydrite crystal

Figure 15: pronounced dissolution patterns of calcite after 14 days.

Figure 16: Growth of hollow kaolin crystals

Figure 17: changes in the brine chemistry of principal ions during the experiment

Figure 18: XRD analysis of the reacted sample

Figure 19a: pronounced dissolution patterns of calcite after 21 days.

Figure 19b: pronounced dissolution patterns of calcite after 37 days.

Figure 20: changes in the brine chemistry of principal ions during the experiment

Figure 21: The domain used to study the vertical migration and distribution of CO₂
Figure 22: Relative permeability curves for the traditional (base-case) simulations and the set for the “permeability jail” case

Figure 23: Vertical distribution of CO₂ (as free gas phase, and in the dissolved state) for the domain with uniform permeabilities and in the system with “permeability-jail” relative permeabilities in the seal.

Figure 24: Vertical distribution of CO₂ (as free gas phase, and in the dissolved state) for the domain with uniform permeabilities and in the system with “permeability-jail” relative permeabilities in the seal. The seal permeability is 1 md in all the simulations.

Figure 25: Photographs of San Juan basin core taken from the Carson Federal G #1 well

Abbreviations

CO₂: carbon dioxide
SO₂: sulphur dioxide
µm: micrometers
IPCC: inter governmental panel on climate change
GHG: greenhouse gas
Ppm: parts per million
EOR: enhanced oil recovery
psi: pounds per square inch
m: meters
C: Celsius
g: grams
K: Kelvin
mg/l: milligrams per liter
XRD: X-ray diffraction
SEM: scanning electron microscope
EDS: energy dispersive X-ray spectroscopy
ICPMS: inductively coupled plasma mass spectroscopy
IC: ion chromatography
H₂SO₄: sulfuric Acid
DH: debye huckel equation
md: milli darcy
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