Carbon Dioxide Sequestration: Effect of the Presence of Sulfur Dioxide on the Mineralogical Reactions and on the Injectivity of CO₂+SO₂ Mixtures

Topical Report

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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 formation 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 formations, since saline formations 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 the presence of SO₂ change the base mineralogical sequestration reactions? This question was addressed by performing high-temperature, high-pressure sequestration reactions with and without the presence of SO₂.

2. Does the presence of SO₂ affect the injectivity of CO₂ and SO₂ mixtures? An experimental system was designed and assembled during this project period.

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 formation.

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, re-precipitation causes the calcium ion concentration to decrease. The presence of SO$_2$ 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 CO$_2$. These processes also affect the porosity and permeability of the system. Locally, changes in porosity and permeability can affect the injectivity of CO$_2$.

An experimental system was designed and assembled to study changes in injectivity with and without the presence of CO$_2$. The experimental system consists of two precision high-pressure pumps capable of injecting liquid and gases at predetermined rates into cores at formation conditions.

The manner in which CO$_2$ distributes itself in the reservoir is also important in determining the distribution of CO$_2$ 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 CO$_2$ more effectively.
Background

Carbon dioxide (CO₂) is the most abundant (64%) greenhouse gas (GHG). The atmospheric concentration of CO₂ 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 CO₂ emissions are from power plants which account for about 40% of the total emissions (IPCC 2007). Carbon dioxide sequestration appears to be an important potential method by which emissions into the atmosphere can be reduced. In this method, anthropogenic CO₂ is injected into geologic formations such as saline formations, depleted oil reservoirs (CO₂ enhanced oil recovery) and unmineable coal seems (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 CO₂ deep underground is particularly promising because deep sedimentary formations have the potential to retain CO₂ in the subsurface for thousands to millions of years (Bachu 2002). In the United States, the capacity of deep saline formations is greater than any other geologic formation with very high estimates (U.S. Department of Energy, 2007, 2008, 2009), and they are also found within close proximity to power plants. Formations 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 CO₂.

The temperature in these formations (50°C-80°C) varies greatly depending on the depth and also the local geothermal gradients (Bachu 2002). Typically, CO₂ is injected at depths greater than 800m to ensure that it stays in the super critical state (critical temperature and pressure of CO₂ are 31°C and 1073 psi, respectively) (Span and Wegner 1996). The notion of CO₂ disposal in formations has been discussed in the literature with specific formations 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). The comprehensive Carbon Sequestration Atlas (U.S. DOE, 2007 and 2008) provide up-to-date information on capacities in the United States and Canada.
Geologic formations, which are artificially charged with CO₂ are called carbon repositories (Kaszuba et al. 2005). Once injected CO₂ 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 CO₂. Subsequently, depending on a rate controlled by several factors such as the rate of CO₂ injection, the rate of CO₂ dissolution into the pore water, the surface area available for the reaction and the rate of diffusion of the CO₂ into the pore water away from the pore water-CO₂ interface, CO₂ dissolves in the formation water. This process is termed solubility trapping. With time CO₂ is trapped as a discontinuous phase (either in supercritical form or as dissolved CO₂) in the pores of a formation leading to capillary trapping. CO₂ forms carbonic acid, which dissociates to form carbonate and bicarbonate ion leading to ionic trapping of CO₂. 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 CO₂ (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 CO₂ 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 CO₂. They reported the precipitation of magnesite, siderite and analcime. Kaszuba et al. (2005) then carried out a study to analyze the effect of CO₂ 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 CO₂ to gravity migration with subsequent release through sub vertical fractures and faults. Few experimental studies examined geochemical reactions in a saline formation in response to CO₂ 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 formation (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 SO₄⁻ on geochemical reactions and the solubilities and porosities of the repository.

**Objectives**

The objectives of this project were as follows:

1. Develop an experimental assembly to analyze CO₂, brine and rock interactions.
2. Develop an understanding on the effect of the presence of SO₂ in the CO₂ stream during sequestration on the mineralogical reactions in saline formations.
3. Study the effects of the presence of SO₂ on the injectivity of CO₂ in formations.
4. Evaluate the effects of different seal properties on vertical migration of CO₂ in formations.

**Experimental Methods**

**Mineralogical Reactions**

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>NaₓCaᵧAlSi₂O₈</td>
<td>CaMg(CO₃)₂</td>
<td>(Fe, Mg, Al)ₓ(Si, Al)₄O₁₀(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 a 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 2. Initial composition of the brine for all the experiments (<=detection limits).

<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.

![Schematic diagram of the experimental setup.](image)

**Table 3. The conditions adopted for each of the 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 inductively coupled plasma mass spectrometry (ICPMS) and dissolved anions by ion chromatography.

**Injectivity studies**

The experimental setup consists of three dual cylinder Quizix pumps for CO₂, brine and the fluid for the overhead burden (Figure 2). The flow is regulated using high-pressure gate valves rated to 15000 psi. All the pumps are automated; the flow is controlled via pump-works software. The flow of the CO₂ and brine is directed to a core holder where the absolute and the differential pressures across the core are measured using sensitive pressure transducers. The brine after the breakthrough is collected on a digital scale and preserved for analysis. The whole assembly is mounted in a well-insulated oven maintained at 100°F.
The experimental system was built, tested and evaluated for experiments. Special provisions were necessary for injecting SO$_2$ into the system. However, the effort required to accomplish this was more extensive than originally anticipated. The proposed injectivity studies are being performed under separate funding, and the results will be published as they become available.

**Vertical migration studies**

For all simulation experiments, the TOUGHREACT simulator was utilized (Xu et al., 2006), which includes full thermal-hydrologic-chemical coupling – multiphase CO$_2$ 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 CO$_2$ 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- CO$_2$-SO$_2$ 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 vertical migration studies were performed by using a multiphase flow simulator (TOUGHREACT) with different seal properties.

**Results**

**Mineralogical reactions**

*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 3a) and illite (minor quantities) (Figure 3b) 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 4 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 3a: SEM image of the host rock at 1kx magnification showing plagioclase feldspar deposits on quartz

Figure 3b: SEM image of the host rock at 1kx magnification showing branched aggregates of plagioclase feldspar and minor quantities of illite
**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 CO₂ 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 identify 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. 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 (Table 4). The precipitation of quartz was not conclusive since the change in its composition was within the uncertainty in measurement with XRD. The patterns of XRD analyses of pre and post reaction sample are superposed in Figure 5. Figure shows precipitation of halite and calcite.

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 6a, 6b). 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 deposited on the reacted surface (Figure 6c). 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 6d). The source of iron for ankerite was the dissolution of chlorite, 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 5: 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 6a: SEM image at 6kx magnification showing growth of calcite as layers
Figure 6b: SEM image at 12kx magnification showing precipitation of calcite aggregates on quartz.

Figure 6c: SEM image at 3kx magnification showing deposition of Halite chunks.
Figure 6d: SEM image of Ankerite growth in the final sample

Experimental set B (100°C and 2000 psi). The experiments were carried out with the same experimental setup used for the Set A experiments with CO₂ 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. However as the pH increases to pH of about 7 the \( \text{H}_4\text{SiO}_4 \) 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 7 (7a 7b 7c) 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 7b 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 7c (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 8a) are highly irregular in shape and show no consistency in size. One calcite crystal had a width of about 10 μm 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 7d 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 (Figure 8b). The growth was seen as aggregated units in the interstitial spaces between the primary minerals, especially quartz. Figure 9 confirms the precipitation of ankerite through EDS analysis.
Figure 7a: SEM image showing calcite in the initial samples

Figure 7b: SEM image showing calcite in the sample showing dissolution after 62 days
Figure 7c: SEM image showing the growth of calcite after 134 days indicative of mineral precipitation reactions.

Figure 7d: SEM image showing the growth of new phase probably analcime on the surface.
Figure 8a: Calcite crystals growing in interstitial spaces between plagioclase feldspar

Figure 8b: Kaolinite deposition on quartz
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 10). 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 10: Changes in concentrations of the principal ions during the experiment

Figure 11 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).
Figure 11: Rock chemistry results corroborated with brine chemistry

**Experiment Set C (100°C and 600 psi).** 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 (Table 7). 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 (Figure 12). 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 8). 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: 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>
</tr>
</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>
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<td>37</td>
<td>10599</td>
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<td>4</td>
<td>19</td>
<td>994</td>
<td>34.8</td>
<td>1551</td>
<td>37157</td>
</tr>
</tbody>
</table>

Table 8: 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>

Figure 12: XRD analysis of the reacted sample
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 9). Conclusions regarding 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 9: 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>22</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 (Figure 13). 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.
Figure 13a and 13b: Growth of anhydrite crystals 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 2kx 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 (Figure 14). 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 15a). 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.

Figure 14: EDS analysis confirming the growth of anhydrite on anorthite and quartz
There were pronounced dissolution patterns for most of the primary minerals involved in addition to the precipitation of anhydrite. The calcite chunk in Figure 16 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 17), 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 17 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.

Figure 16: pronounced dissolution patterns of calcite after 14 days
The presence of SO$_2$ in the feed gas stream along with CO$_2$ alters the brine chemistry to a great extent (Figure 18). 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
CaSO₄). 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 18: changes in the brine chemistry of principal ions during the experiment

**Experiment set D (100°C and 2000 psi).** These experiments were performed at an initial pH of 3 by acidifying the brine with 0.1ml 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 Figure 19 and 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 (Figure 20). Brine chemistry also supports this (Figure 21). The concentrations of the principal ions increase indicating that the carbonate minerals are undergoing dissolution during the course of the experiment.

![Figure 19: XRD analysis of the reacted sample](image)

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>
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<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>

Figure 20a: pronounced dissolution patterns of calcite after 21 days
Figure 20b: pronounced dissolution patterns of calcite after 37 days

Figure 21: changes in the brine chemistry of principal ions during the experiment
Injectivity Studies

The core-scale laboratory flow tests were designed to evaluate the results of explicit processes of reactive transport with matrix chemical diagenesis and associated porosity and permeability changes on CO2 injectivity. Mechanical deformation was not included in this first generation of experiments. 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.

Injectivity studies with CO2 and CO2+SO2 mixtures with the experimental setup described in the Experimental Section were not completed as designing, assembling and testing the state-of-the-art high-pressure, multiphase facility was more extensive than originally planned. They are being performed in the current project phase.

San Juan Basin rock core samples were acquired for laboratory testing (Figure 22). 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. The subject formations for deep saline sequestration testing are the Jurassic-aged Entrada sandstone and the Mississippian-aged Leadville limestone. The core samples were analyzed for fractures and other heterogeneities. 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, Inc. and performed repeated mineralogic and hydrologic (porosity and permeability) analyses of the cores (Table 12).
<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>

Figure 22. Photographs of San Juan basin core taken from the Carson Federal G #1 well
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 CO₂ in the formation and the parameters that control the migration and subsequent distribution of CO₂ in the various phases.

All of the simulations were performed using TOUGHREACT. The domain used in the simulations is shown in Figure 23, and the general conditions of simulations are summarized in Table 13. 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 24.

Distributions of free and dissolved CO₂ concentrations are shown in Figure 25. In the uniform permeability case, the free-CO₂ concentration is highest at the top of the formation. If the top of the formation is breached, the CO₂ 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 CO₂ is better distributed in the aqueous phase as well.
Figure 23: The domain used to study the vertical migration and distribution of CO$_2$

Table 13: Simulation conditions for the study of vertical migration

<table>
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<th>Parameter</th>
<th>Values</th>
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</thead>
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<td>Grid</td>
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<tr>
<td>Grid block size</td>
<td>100ft<em>10ft</em>10ft</td>
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<tr>
<td>Model size</td>
<td>100ft<em>600ft</em>600ft</td>
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<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>$2.3177\times10^3$kg/hr</td>
</tr>
<tr>
<td>Injection period</td>
<td>258.4 days</td>
</tr>
</tbody>
</table>
Figure 24: Relative permeability curves for the traditional (base-case) simulations and the set for the “permeability jail” case.

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 26).
Figure 25: 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 26: 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.
Conclusions

Mineralogical Reactions. In all of the experiments, changes in mineralogy were evident, and in general, observations of changes in rock chemistry mirrored those seen in brine. In experiments with CO₂, one of the most important conclusions was the observation of calcite re-precipitation. This indicated that permanent mineralogical sequestration is possible. Chlorite dissolution and analcime and ankerite precipitation were common features in all CO₂ experiments. In experiments containing SO₂, the mineralogical reactions were significantly different compared to experiments where only CO₂ was used. The dissolution patterns continued and no calcite re-precipitation was observed. The most significant findings in these experiments were the precipitation of anhydrite, gypsum and bassanite. These results are highlighted in Mandalaparty et al. (2009).

Vertical Migration and Seal Properties. The distribution of CO₂ in the free gas and dissolved forms in a layered reservoir depends on the absolute permeability of the seals, and also on the relative permeabilities employed.

Acknowledgement

This material is based upon work supported by the Department of Energy under Award Number DE-FC26-06NT42808.

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Figure 26: 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.

**Abbreviations**

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

References


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