Laboratory Study of the Influence of scCO₂ Injection on Metals Migration, Precipitation, and Microbial Growth

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Abstract

Laboratory experiments were conducted to evaluate the impact of supercritical carbon dioxide (scCO₂) injection on aqueous and solid phase geochemistry, and subsequent changes in permeability. These experiments showed that brine displacement from the Mount Simon Sandstone cores (~1200 m depth) by scCO₂ was inefficient by advection, because the low viscosity scCO₂ flows predominantly in larger pores, leaving a significant amount of brine in smaller pores. Acidification caused by scCO₂ injection resulted in significant increases in Mg²⁺, K⁺, Na⁺, SO₄²⁻, Al³⁺, and silica concentrations are likely from differing rates of carbonate, clay, albite, and K-feldspar dissolution. The mass of precipitates that formed over 1.2 years (NaCl, KCl, lead oxide, and forsterite) was small, as observed by electron microprobe analysis and did not influence permeability. Trace metals that increased during scCO₂ injection included Ba, Mn, Sr, Ni, Sn, Bi, Cu, Li, P, and Zn, and trace metals that decreased included Hg, Pb, and Co. The scCO₂ injection experiments also showed a moderate amount of particulate (iron oxide) movement correlated with the fraction of scCO₂, but the sandstone permeability did not change, even after substantial (i.e., 115 pore volumes) scCO₂ injection. Anaerobic and aerobic microbial growth was observed (23 and 14 times, respectively) correlated with higher scCO₂ concentration, but the calculated change in pore space occupied by the increase in biomass is insignificant. The small observed geochemical and microbial changes are not expected to reduce the ability to inject scCO₂ into the reservoir, but significant increases in trace metal concentrations could magnify the water quality impact of a potential leak of reservoir fluids into an overlying aquifer.

Keywords: carbon storage, saline aquifer, mineral dissolution-precipitation, microbial growth, particulate movement

1. Introduction

Geological carbon sequestration (GCS) is a promising way to store carbon dioxide (CO₂) over a geologic time scale and mitigate increases in atmospheric CO₂ concentration. Thus GCS is being studied as a means to address global climate change concerns related to coal-fueled energy production (Shaffer, 2010; Szulczewski et al., 2012). The U.S. Department of Energy (DOE) proposed FutureGen 2.0 site (Jacksonville, Illinois) is designed to demonstrate the technical feasibility of permanent storage in a deep geologic formation at a 1219 m depth (Bonneville et al., 2013, Vermeul et al., 2014). The moderately permeable, brine-filled upper Mount Simon Sandstone formation at the storage site was selected as the primary CO₂ injection and storage reservoir for the proposed project. This reservoir is overlain by the Eau Claire formation, which forms the primary confining zone at the site.

During supercritical CO₂ (scCO₂) injection, in situ brine is displaced. Pore water acidification due to scCO₂ injection induces mineral dissolution and may result in porosity and permeability changes in the storage formation (Lamy-Chappuis et al., 2014; Tutolo et al., 2014; Luhmann et al., 2014). The scCO₂ injection may also mobilize colloidal particles in the formation (Izgec et al., 2008), and the subsequent filtration and deposition of these particles can significantly change the permeability of the formation (Shapiro et al., 2007; Moghadasi et al., 2004). In addition, dissolution could result in direct movement of hematite particulates/colloids or clays, potentially clogging downstream pores (Lu et al., 2011, Scheffer, 2012). Increases in trace metal concentrations from acidification are also likely, and although these changes would not influence permeability, degradation of the water quality in the injection zone is of significance because of the possibility of a leak into an overlying drinking water aquifer.

In addition to acidification, scCO₂ injection also alters the geochemical equilibrium between the rock and pore water due to changes in water content, pressure, and multiphase fluid permeability, resulting in a series of interactions for the system to reach a new equilibrium state. A study of the geochemical reactions and processes among scCO₂, brine, and host rock under storage reservoir pressure and temperature conditions showed a decrease in the pH of brine, and that the kinetics of the reactions among scCO₂, brine, and rock were relatively rapid (Kaszuba et al., 2003). Reactions between scCO₂ and storage reservoir rock can also release toxic metals (Spangler et al., 2009; Kharaka et al., 2009; Wigley et al., 2012) and organic compounds

(Kharaka et al., 2009; Zhong et al., 2014) that can migrate away from the reservoir and potentially contaminate the overlying aquifer. Injection of the scCO₂ into a deep saline reservoir may induce metabolic changes in the microbial communities (Morozova et al., 2010). The interest in trace metals is related to the potential for degradation of water quality within overlying aquifers in the event of an unforeseen leak. Macroelements present in the fly ash include Al, C, Ca, Cl, Fe, Mn, N, Na, P, S, Ti, and K (Bhangare et al., 2011, Reddy et al., 2005, Levy et al., 2002). Particulate components (trace elements) that may be present in fly ash, even in advanced coal plants, include As, B, Cr, F, Mn, Ni, Pb, Hg, Se, V, and Zn (Meij and Winkel, 2004). Although the aquifer is likely reducing, large scCO₂ injection with O₂ may eventually overwhelm aquifer reductive capacity, which could cause changes in metals mobility or microbial activity. Redox reactive metals such as Fe, As, and Mn are more mobile in a reducing environment and will be less mobile (precipitate) in an oxic environment.

Microbial activity at the interface of aqueous phase CO₂ under supercritical conditions has been observed (Peet et al., 2015). Changes in pore water pH, temperature, salinity and other abiotic factors associated with scCO₂ injection may affect the microbial growth of the significant in situ population near the injection well. Furthermore, the possible impact of geologic carbon sequestration injection on the microbial community may also affect biofilm formation and change the permeability of the storage formation, which, over time, may influence further scCO₂ injectability (Scheffer, 2012). Even if microbial growth does not alter the permeability, the presence of microbes can still alter the rate of calcite dissolution (Luttge and Conrad, 2004, Warren et al., 2001, Jacobson and Wu, 2009).

The focus of this study was to evaluate changes in aqueous and solid phase geochemistry from scCO₂ injection, and secondary effects of permeability changes caused by precipitates, particulate movement, or microbial growth. Aqueous trace metal mobility change was also evaluated because of the water quality impact. These scCO₂-brine-sandstone interactions could lead to: a) a decrease in some major ion concentrations (i.e., carbonate precipitation) resulting in a decrease in permeability, b) substantial microbial growth resulting in a decrease in permeability or sufficient microbial growth to influence calcite precipitation, c) mineral dissolution and an increase in permeability, d) particulate/colloid movement in the acidic environment altering permeability, and e) an increase in trace metal concentrations that alters water quality. The immiscible scCO₂ displacement of the brine was also evaluated to some extent, as it influences

brine-rock interaction rates. It is hypothesized that metals present as cations (in the brine or scCO₂ or desorbed or from mineral dissolution) will remain mobile or be mobilized because the scCO₂ creates an acidic environment. Metals present as oxyanions would likely become less mobile. Changes in the redox environment from the injection of trace oxygen in the scCO₂ into the anoxic/reducing environment of the natural sandstone would decrease Fe, Mn, As mobility but increase the mobility of other metals (including Cr, U). The displacement of brine by injected scCO₂ into sandstone cores and the displacement of scCO₂ by injected brine was evaluated in flow-through columns under aquifer temperature (38°C) and pressure (10.3 to 12.4 MPa). Long-term geochemical reactions were studied in stop-flow columns (containing sandstone cores) for times ranging from days to 1.2 years. Microbial growth was also evaluated in stop-flow column incubation tests using rock core interacting with scCO₂. The mobilization of particles was quantified by brine/scCO₂ injection into sandstone cores and capturing particulates in a downstream secondary column. Formation permeability change was monitored by measuring the pressure drop difference when water was injected through the sandstone cores before and after reacting with scCO₂.

2. Material and Methods

2.1. Materials

The upper portion of the brine-filled Mount Simon Sandstone is a large-scale (i.e., 10s to 100s of meters) marine depositional environment that resulted in interbedded sandstone, shale, and limestone as the shoreline transgressed or regressed, because coarser grained particles are deposited near the shore. This formation is composed of 96.2% quartz, 1.8% mica, 1.2% mullite (Al₆Si₂O₁₃), and 0.76% hematite (Fe₂O₃). The upper Mount Simon has a mean porosity of 0.201, average dry bulk density of 2.34 g/cm³, and a mean intrinsic permeability of 1.42 x 10⁻¹⁴ m². In comparison, the intrinsic permeability of the lower Mount Simon Sandstone and overlying Eau Claire Formation was one or more orders of magnitude less.

In cores collected from the upper Mount Simon aquifer at 1204 m bgs, fine-scale (sub-mm) variability is observed with coarser (~0.3 mm) and finer (~0.13 mm) grain sizes, iron oxides between the two layers, and widespread abundance of orthoclase in coarser layers (Figure 1). The ferric iron oxides may be secondary deposits, hence not part of the original depositional

environment. Electron microprobe analysis was conducted on thin sections from the 1204 m depth for analysis of crystalline phases. This consisted of collecting Si, Al, K, Na, Ca, Cl, Fe, and Mg elemental maps 12 by 12 mm in size (1500 by 1500 points, 2-micron pixel resolution) using a JEOL JXA-8230 electron probe microanalyzer.

Figure 1. Upper Mount Simon core from 1204 m depth with fine-scale variability in sand size and red (ferric) iron oxides: a) cross-section through a 10.2 cm diameter by 15.2 cm length core, and b) 2 cm by 1.5 cm thin section.

Geochemical experiments were initially conducted using intact cores 2.54 cm in diameter by 7.62 to 15.2 cm in length subsampled from the 10.2 to 12.7 cm diameter by 15.2 cm long cores; all cores and cuttings were obtained from the initial stratigraphic borehole. The porosity of cores was measured by weight difference between 65°C-dried cores and water-saturated cores, accounting for the density of the brine. Water-saturated constant flow was used for intrinsic permeability measurements based on pressure difference were conducted at four or five flow rates for each core. Some of the 2.54 cm diameter core subsamples were drilled horizontally through the vertical cores to compare vertical and horizontal permeabilities. Cores were sleeved in Teflon, then epoxied into 3.18 cm diameter stainless steel columns with no end frits.

The pore water in the upper Mount Simon Sandstone Formation is brine with a density of 1.046 g/cm³, composed predominantly of Na⁺ and Cl, with lesser amounts of Ca²⁺, Mg²⁺, and

carbonate (O'Connor and Rush, 2005). The aqueous iron concentration of 18.6 mg/L is likely ferrous iron and reducing conditions exist in the formation. Because dissolved oxygen would be injected as a minor component with the scCO₂, a change to oxic conditions could occur near the injection wells, resulting in geochemical and microbial changes. Synthetic brine composed of several major ions (Table 1, based on analysis of the upper Mount Simon brine) and trace metals was used in the geochemical and microbial experiments. The synthetic scCO₂ injection mixture consisted of scCO₂ (97%), inert elements (N₂, argon, 2%) oxygen (0.002%), NO_x (0.12%), and SO_x (0.12%). Trace metals/compounds potentially present in the scCO₂ injection solution previously noted in emissions from modern coal-fired power plants include Mn, Mg, Co, Ni, B, Mo, P, Zn, Se, Fe, NH₄, Ca, Cr, As, Pb, V, Hg, Al, Ti, K, and S (Meij and Winkel, 2004; Rizeq et al., 1994). These trace metals were added to some experiments in the synthetic brine to evaluate change in their mobility (Table 2).

Table 1. Major chemical concentrations in synthetic brine.

compound (mg/L)	conc.
NaCl	59440
CaCl ₂ •2H ₂ O	9884
MgCl ₂ •7H ₂ O	10820
KCl	269
NaF	185
FeCl ₂	54.3
Na ₂ CO ₃	166
SiO ₂ •2H ₂ O	37

Table 2. Trace metals and concentrations added to synthetic brine.

compound	conc. (mol/L)
MnCl ₂	3.97E-08
CoCl ₂	3.85E-08
NiCl ₂	1.16E-07
H ₃ BO ₃	2.43E-06
Na ₂ MoO ₄	2.43E-08
NaH ₂ PO ₄	2.08E-06
ZnCl ₂	1.83E-07
Na ₂ SeO ₃	2.89E-07
NH ₄ Cl	5.60E-03
NaHAsO ₄	1.00E-06
NaCrO ₄	4.35E-07
PbCO ₃	1.87E-08
V ^{III} Cl ₃	1.00E-06
HgCl ₂	1.84E-08

2.2. Experimental Setup and Procedures

2.2.1. Fluid Displacement

The displacement of the brine by scCO₂ was investigated in stainless steel columns containing intact sandstone (2.54 cm diameter by 12 to 15 cm length) or sandstone material (2.54 cm diameter by 30 cm length). The columns were placed in an oven (38°C) and the inlet and outlet were connected to separate ISCO piston pumps. One pump was used to inject fluid at a specified flow rate (0.01 to 5 mL/minute) to the inflow end and the second pump used to maintain the outlet pressure during fluid displacement (10.34 to 20.68 MPa). Heat tape with a temperature control unit was also used on the injection pump and inlet tubing. The columns were then saturated with brine. The scCO₂ of a specific volume was then injected into the column to displace brine to evaluate brine displacement as a function of the volume of scCO₂ injected. The weights of column with dry packed sandstone, with saturated brine, and at multiple times during displacement tests were measured to calculate the residual water saturation over a range of pore volumes of scCO₂ injection using the following relationship:

$$\text{Fluid 1 Fraction (by volume)} = [M_{\text{tot}}/V_{\text{tot}} - \rho_2]/[\rho_1 - \rho_2] \quad (1)$$

where M_{tot} = the total void mass (total mass – empty core mass), V_{tot} = total pore volume, ρ_1 = fluid 1 density (g/cm³), and ρ_2 = fluid 2 density (g/cm³), assuming constant temperature and

pressure. During field scCO₂ injection, brine is generally displaced by scCO₂. Displacement experiments were conducted to characterize the residual scCO₂ saturation during brine injection with scCO₂ injection upward and downward in cores to additionally evaluate the effects of buoyancy, which are significant at field scale (Williams et al., 2014).

2.2.2. Rock Core/scCO₂ Geochemical Interactions

Stop-flow column experiments were used to study the geochemical reactions over time between brine, scCO₂ and the sandstone, with measurement of aqueous pH, electrical conductivity, and major cation/anion changes. A range of brine/scCO₂ ratios was used to approximate the fluid composition at different distances from the injection well and at different injection times. Compositions of 10, 30, 50, 70, 90, 97, and 100% scCO₂ (with a balance of volume brine) were used in different experiments. Brine and scCO₂ was injected into these columns containing intact cores or core material, but experiments have no flow over most of the reaction time. In a few of the continuous flow fluid displacement experiments (Section 2.2.1) pH, electrical conductivity, and major ions were measured. However, the short (i.e., hours to 10s of hours) time scale of those experiments limited geochemical changes. At specified times ranging from days to 1.2 years, the aqueous fluid in the column was sampled for geochemical changes. Aqueous samples were collected by connecting an empty column to the outlet of the stop-flow reactor column, injecting a specified volume (~5 pore volumes) of deionized water through the reactor column to advect/dilute fluids into the second column, then lowering the pressure of the second column to then collect the aqueous sample.

Aqueous samples were measured for cations, anions, pH, and specific conductance. Pore water major and trace cations/elements (Ca, Na, K, Mg, Fe, P, Al, Si, Mn, Co, Ni, B, Mo, P, Zn, Se, Fe, NH₄, Cr, As, Pb, V, Al, Ti, K, and S) were measured using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin-Elmer Optima 2100DV). Mercury was measured using an inductively coupled plasma mass spectrometer (ICP-MS). These elements were predominantly present as cations except for Si, which is present as SiO₂ (aq). Aqueous carbonate was measured on a Shimadzu carbon analyzer. Six anions were measured using a Dionex ICS 2000 ion chromatograph (F⁻, Cl⁻, NO₂⁻, Br⁻, SO₄⁻², NO₃⁻). Aqueous ferrous and total iron was additionally measured by a colorimetric ferrozine method (Gibbs, 1976). Measurement of the pH of the scCO₂/brine system at low water content and high pressure was accomplished by

dissolution of the system (100x) with deionized water in order to maintain most of the carbonate partitioned in the water. The specific conductance of the aqueous solution was also measured on diluted samples. Reported pH and specific conductance measures were corrected for dilution.

2.2.3. Permeability Measurements and scCO₂ Injection

In this study, intrinsic permeability was measured using brine as the fluid to assess whether sandstone permeability would change appreciably due to mineral-phase dissolution/precipitation and/or particulate advection. At field scale, as the scCO₂ saturation increases and brine saturation decreases, the equivalent hydraulic conductivity of the formation will increase because of the significantly lower viscosity of the scCO₂ compared to water. Although this fluid change is likely to dominate the overall hydraulic response, this study was conducted to investigate whether the precipitation or movement of iron oxide particulates have the potential to change formation permeability to some extent. The intrinsic permeability was measured by injecting brine through the cores and measuring the pressure decrease from inlet to outlet of the core at four to five different flow rates for a total of 17 cores in the upper Mount Simon Sandstone and shale from the Eau Claire formation that forms the primary confining zone. For two cores, the intrinsic permeability was additionally measured after brine or scCO₂ injection (from 5 to 110 pore volumes). The 100% brine saturation was needed for these measurements, so after experiments with mixed brine/scCO₂ solutions, the core pressure was dropped to outgas scCO₂ and 20 to 30 pore volumes of brine were injected to brine saturate the cores. Brine saturation was checked by comparison to initial 100% brine core weight. These columns had no outlet frits and used larger diameter (1.59 mm internal diameter) tubing to minimize pressure buildup related to particulate movement from cores (see following section).

2.2.4. Mobilization of Particles from scCO₂ Injection

Column experiments were conducted using varying rates of acidification induced by different scCO₂/brine ratios and a range of reaction times to characterize the total particulate mobilization. Mount Simon Sandstone cores were placed in stainless steel columns. No frits were placed at the effluent end of the columns to interfering with the flow of mobilized particulates. The columns were connected to a second column filled with 0.3 mm glass beads and 1 µm outlet frit. The mobilized particulate weight was determined by monitoring the weight change of the glass bead column. These experiments were conducted with different fractions of

scCO₂ (0, 10, 30, 50, 70, 90, 95, 98, and 100%) for 500 h of reaction time, before injecting 1 to 35 pore volumes of brine.

2.2.5. Microbial Biomass and Growth in Brine/scCO₂ Mixtures

Microbial growth experiments consisted of reacting aseptically collected core chips from the center of intact cores (i.e., cores were processed in an attempt to obtain representative samples of the native microbial community) with a mixture of aquifer brine, scCO₂, and trace components with no flow in a column reactor set at 12.41 MPa pressure and 38°C temperature for times ranging from 10 to 2200 h. Experiments were conducted at brine/scCO₂ ratios of geochemical experiments (Section 2.2.2). In a control experiment, core chips was mixed with brine only (no CO₂ or trace components added) and held at 12.41 MPa pressure and 38°C, representing the environment in the reservoir with no CO₂ injection. Bacteria growth in systems of brine and scCO₂ with and without minor components was compared to evaluate the influence of the trace constituents. The microbial population was measured at the end of each experiment using standard culturing methodologies to characterize the amount of growth.

Because microbes attach strongly to sediment surfaces, the procedure for counting the microbial population involves 1) using a high-ionic-strength solution and shear forces to detach microbes from the core pieces, 2) mixing the solution with a DNA stain, 3) filtering a specified amount of the solution containing fluorescent-DNA-stained microbes onto a microbial filter, and 4) counting the number of bacteria on the filter. The phosphate-buffered saline solution consisted of 0.798 mol/L Na₂HPO₄ and 0.15 mol/L NaH₂PO₄ at pH 7.5. The core pieces (2 g) were mixed with 20 g of the phosphate solution to detach microbes from surfaces. A preliminary series of experiments was conducted at different sediment/phosphate solution ratios to determine a mixture that worked best. A DAPI (4',6-diamidino-2-phenylindole) fluorescent DNA stain (250 µL in 20 mL) was then added to the solution. This core/phosphate solution was reacted for 30 minutes in the dark (DAPI stain is light sensitive), then vortexed for 1 minute to create high shear conditions to detach microbes from the sediment surface (along with the high-ionic-strength phosphate solution). Then, 2 mL of this solution was filtered onto a microbial filter, which consisted of a Whatman 25 mm GF backing filter and 25 mm black polycarbonate microbial filter (0.2 µm) (from General Electric 1215609 or Nucleopore PCMB). Four milliliters of filtered deionized water were then washed onto the vacuum filter system to remove excess

DAPI stain that was not attached to microbes. The filter was then mounted onto a glass slide; citifluor was added and a cover plate. Slides were counted immediately or stored at -80°C before counting. Counting the microbial biomass involved of the use of a specialized fluorescent light microscope at 1000x magnification. At the correct dilution, the field of view showed fewer than 100 microbes, which were manually counted. A total of 10 different fields were counted to obtain a statistical distribution of the counts. If the microbial density was too high, dilutions from the original extraction solution were used until the desired microbe density for counting was obtained.

3.0. Results and Discussion

3.1. Displacement of Reservoir Fluids

Geochemical changes in the sandstone-brine-scCO₂ system are influenced by the presence of the multiple liquid phases and slow mixing between scCO₂ and brine. Experiments injection of scCO₂ into brine-filled cores and injection of brine into scCO₂-filled cores were conducted to evaluate fluid mixing for subsequent geochemical experiments. The displacement of brine by scCO₂ was inefficient and incomplete, as shown by residual brine saturations greater than 50% even after more than 100 pore volumes of scCO₂ were injected. The scCO₂ was more readily displaced by brine (38°C, 12.71 MPa). With 25 pore volumes of brine injection, the residual scCO₂ saturations were lower than 30% (Figure 2a). This inefficient displacement of brine by scCO₂ in sandstone is similar to experimental results previously reported (Perrin et al., 2009 in Figure 2a). Residual water saturation experiments were also conducted at 10.34, 15.17, and 20.68 MPa pressure, which are all in the scCO₂ region, but CO₂ density changes significantly at these different pressures (Szecsody et al., 2014). There was no observable trend in residual water saturation in response to the different pressures.

The displacement of brine by scCO₂ is unfavorable because brine has a much higher viscosity (about 0.7 mPa·s at 38°C) than scCO₂ (0.06 to 0.1 mPa·s). In addition, because water has a high affinity for most mineral phases, it is predicted that injected CO₂ with a ~10x lower viscosity would displace brine in larger pores, but there would be some residual water saturation in smaller pores. This would result in significant viscosity fingering during the displacement in the cores (Homsy, 1987), resulting in an inefficient brine fluid displacement. A number of

experimental and/or simulation studies of scCO₂ displacement of water in porous media (Pruess et al., 2003; Juanes et al., 2006; Ahmadlouydarab et al., 2012; Pruess and Garcia, 2002; Bennion, 2008; Suekane et al., 2005; Williams et al., 2014) described 1) residual water saturation, 2) heterogeneous flow (i.e., CO₂ fingering), 3) redistribution of scCO₂ due to buoyancy, and 4) redistribution of water once flow stops result in discontinuous CO₂ zones. Smaller pores tended to contain water, with an occasional flow of a CO₂ bubble (Suekane et al. 2005). Experimentally, effects of fingering during brine injection into scCO₂-filled sandstone left considerable scCO₂-filled pores, even after 20 pore volumes (Figure 2a, triangles). After 1 pore volume of brine injection, the brine saturation in three experiments averaged 40%; after 10 pore volumes of brine injection, brine saturation ranged from 48% to 68%; and after 20 pore volumes of brine injection, brine saturation ranged from 58% to 78%. Therefore, there is considerable heterogeneity in the upper Mount Simon Sandstone, even at a small (cm) scale, which leads to non-uniform displacement of fluids, regardless of whether the fluid properties of the injectate are favorable for displacement of the initial fluid.

Figure 2. Residual fluid saturation in sandstone core after a) scCO₂ displacing brine (diamonds, flow upward) and brine displacing scCO₂, (red triangles, flow upward), and b) buoyancy effects of upward scCO₂ injection into empty column (squares) or upper Mount Simon Sandstone cores with flow downward (blue circles) or upward (diamonds). In (a), scCO₂ displacing brine from Perrin and others (2009) shown (circles).

Because the scCO₂ has a density of ~0.7 g/cm³ (12.41 MPa, 38°C) and the injection formation brine density is 1.0456 g/cm³, the scCO₂ will migrate upward over time the time scale of years to 10s of years in porous media depending on formation permeability (Williams et al.,

2014). The buoyancy effect has also been demonstrated experimentally in this study. The scCO₂ migration from advection (i.e., injection) or buoyancy is also highly influenced by the large viscosity difference between the scCO₂ (0.07 mPa·s at 12.41 MPa, 38°C) compared with the brine (0.68 mPa·s). When scCO₂ was injected into the bottom of an empty column (i.e., flow upward), the scCO₂ immediately flowed to the column outlet and out of the column (Figure 2b, squares). Even after 2 pore volumes of scCO₂ injection, the brine saturation was still 0.98 to 1.0, because the buoyancy-driven scCO₂ flowed through the brine and left it in the column. In contrast, with the column containing an upper Mount Simon Sandstone (average pore size 0.01 to 0.04 mm), with flow upward, after 20 pore volumes of scCO₂ were injected triangles in Figure 2b), some brine was displaced, but the brine saturation was still 65%, because preferential flow of the scCO₂ was dominantly through some pores dominated flow and effects of buoyancy were minimal. With the same column and injection of the scCO₂ downward in the column (i.e., so there would be no influence of buoyancy), the change in brine saturation was the same (diamonds, Figure 2b) as it was for the upward flowing orientation. These two experiments show that for the time scale of these experiments (< 6 h), there is no influence of buoyancy on scCO₂ transport through the fine sandstone, even though field-scale simulations predict significant effects of buoyancy over years to 10s of years (Williams et al., 2014).

3.2. ScCO₂ Injection and Indicators of Dissolution: pH and Specific Conductance

Under aquifer conditions of 38°C and 12.41 MPa, a considerably greater amount of CO₂ gas is soluble in aqueous solution, which results in a decrease in pH and increase in specific conductance. Acidic conditions can lead to desorption of cations and dissolution of some sediment minerals such as quartz and clays, resulting in additional aqueous ions. Simulation of the theoretical pH of an aqueous solution that would result from incorporation of carbonate under different pressures (Figure 3) shows in this case that the initial brine at pH 7 decreased to pH 2.9 at 12.41 MPa using Geochemist Work Bench 10.0. This simulation assumes buffering from aqueous carbonate species but no buffering from mineral dissolution/precipitation. In a real system with a very high sediment/water ratio (i.e., porosity is 15% for the upper Mount Simon Sandstone), there would be considerable buffering capacity due to mineral dissolution and precipitation. Experimentally, the pH did become more acidic with increasing partial pressure of CO₂, but not to the extent of the simulation (Figure 3) as the simulation did not include buffering

effects from the sandstone. In contrast, the solution specific conductance of the solution increased as a function of the CO₂ partial pressure.

Figure 3. Influence of scCO₂ on pH (calculated with solid line, experimental with diamonds) and specific conductance as a function of pressure (red triangles).

The difference in total carbonate ion concentration at standard atmospheric conditions is influenced by multiple factors, including: 1) calcite solubility increase with pressure, 2) calcite solubility increase with salinity, 3) calcite solubility decrease with temperature, 4) increased carbonate solubility in aqueous solution with pressure, 5) carbonate solubility decrease with increasing salinity, and 6) carbonate solubility decrease with increasing temperature. The most significant factors are the increase in CO₂ gas solubility with increasing pressure, and decreasing CO₂ gas solubility with increasing temperature and salinity. The CO₂ gas solubility in subsurface conditions (12.41 MPa, 38°C, 50,000 mg/L salinity) is 2567 times higher than at 1 atmosphere, 38°C, and low ionic strength (Jarrell et al., 2002; Crawford et al., 1963; Ingle, 1975, Garrels and Christ, 1965). The high salinity resulted in a 22% decrease in CO₂ gas solubility.

The pH measurements for brine/scCO₂ in contact with the sandstone for 100s to 1000s of hours (Figure 4a) showed some acidification, from a value of 7.5 (brine) to as low as pH 4.8 for the experiment containing 97% CO₂ by 100 h, then some pH neutralization at larger times. There was a general trend of greater acidification for systems that contained a greater fraction of CO₂, which is consistent with theoretical predictions (Figure 3). By 10,000 h, the pH had leveled off or neutralized somewhat, likely as a result of precipitation reactions. Most experimental

systems showed a slight increase in aqueous specific conductance (Figure 4b) for the first few hundred hours, then a significant increase at later times. The addition of CO₂ should increase dissolved carbonate, which would result in the observed increase in solution electrical conductivity. The maximum electrical conductivity increase for the change in pressure (Figure 3) shows a 20 times increase from atmospheric conditions to 12.41 MPa by 100 h, whereas by 10,000 h, the 90% and 97% scCO₂ systems showed an additional increase of 15 times greater specific conductance, which indicates significant dissolution may have occurred. The time scale of dissolution indicated by the specific conductance data is 1000s of hours (Figure 4b).

Figure 4. Experimental measurement of aqueous solution: a) pH, and b) specific conductance for different Mount Simon Sandstone-brine-scCO₂ systems. Symbols represent the initial brine (●), 10% scCO₂ (▲), 75% scCO₂ (◆), 90% scCO₂ (○), and 97% scCO₂ (■).

3.3. Aqueous Ion Changes and Implication to Mineral Dissolution/Precipitation

The acidification caused by scCO₂ injection into the sandstone results in short term (< years) mineral dissolution (this section) and long-term carbonate precipitation, with potential changes in permeability (Section 3.5). In addition, while changes in trace metal concentrations (described below) do not alter permeability or impact the injection aquifer water quality, a potential leak into an overlying aquifer could be adversely affected with elevated trace metals. With the introduction of scCO₂ into the saline reservoir (at 38°C and 12.4 MPa), there is a significant increase in the carbonate solubility in aqueous solution and corresponding acidification (pH 3 to 4, Figure 3), which causes short-term desorption of metals and long-term (years) dissolution of mineral phases. Acid treatment of quartz-rich sediments show rapid carbonate and iron oxide dissolution (hours), followed by 2:1 clay dissolution (100s of hours,

Szecsody et al., 2013). Simulation of scCO₂ injection into a sandstone with overlying shale (White et al., 2005) under moderately acidic (pH 4 to 4.8) conditions indicated time scales of dissolution including Na-smectite (10 to 1000 yrs), albite, and K-feldspar (100 to 10,000 yrs), and anorthite (> 10,000 yrs). With eventual pH neutralization, time scales of precipitation were 100 to 10,000 years (kaolinite and dawsonite [NaAlCO₃(OH)₂]), and > 10, 000 years (calcite) [NaAlCO₃(OH)₂]. In a different study, scCO₂ injection in a sandstone dissolved K-feldspar and smectite, and precipitated illite and allophane (Lu et al., 2011). In a field-scale injection into a sandstone aquifer, acidification from the CO₂ injection caused increases in ion concentrations over days to months, likely from rapid carbonate and iron oxyhydroxide dissolution (Kharaka et al., 2006), and long-term albite dissolution (Kharaka et al., 2009). The rapid increase in trace metal concentrations observed in laboratory CO₂ treatment of three sandstones was also caused by carbonate dissolution (with trace metal impurities, Kirsch, 2013). Long-term geochemical experiments with different scCO₂/brine/ Mount Simon sandstone mixtures showed nearly no trend for some major ions in contrast to significant changes for other ions (Figure 5). Measurements of the soluble carbonate in sandstone/brine/scCO₂ experiments confirm rapid carbonate partitioning into the aqueous fluid within 10s of hours, with little change even by 1.2 years (Figure 5d). The amount of carbonate in water was a direct function of the scCO₂/brine ratio, as expected, with a 10 times increase in carbonate for the 10% scCO₂ system, and as much as a 200 times increase in carbonate for the 97% scCO₂ system. The large carbonate increase may have resulted in the precipitation of some calcite, because the soluble calcium decreased over 100s of hours, and generally this effect was greater for the higher scCO₂ experiments (Figure 5a). In contrast, aqueous magnesium concentrations showed nearly no change over 1.2 years, with the exception of some increase for the 90% and 97% scCO₂ experiments (Figure 5b) over 100s of hours, possibly indicating the dissolution of a mafic or clay phase. Silica concentrations initially at 0.3 mmol/L increased as much as 10 times with high scCO₂/brine ratios (Figure 6a), at a time scale of less than 500 h and remained constant over the next 10,000 h. Elevated silica may be caused by clay dissolution over 100s to 1000s of hours (Szecsody et al., 2013), which is more rapid in more acidic environments, and slower albite and K-feldspar dissolution (White et al., 2005). Aluminum concentrations in many cases were below detection limits in the brine, so with the limited reported aluminum concentrations, the Si/Al molar ratios in experiments ranged from 25 to 100 at 72 h, which decreased to 25 by 3 months and to 5.8 by

422 1.2 years (Figure 6b). Clearly, silica-containing minerals other than 1:1 or 2:1 clays dominate
423 dissolution in these systems, and precipitation of Al may be occurring over 100s of hours
424 changing the Si/Al ratio. Other major ions of potassium and sulfate show significant dissolution
425 over 100s of hours (Figure 5c and 5e). The potassium concentration increase may be indicative
426 of K-feldspar dissolution, which is predicted in similar systems (White et al., 2005). Although
427 aqueous sulfate was not expected to change, increases were correlated to the amount of
428 carbonate added (Figure 5e). Sulfate and magnesium increase similarly, possibly indicative of
429 dissolution of specific mineral phase(s). Aqueous sodium was relatively constant over 1.2 years
430 for most cases (not shown), except for the more acidic 97% scCO₂, which showed elevated
431 (2.5x) concentration. This may be indicative of albite dissolution. Aqueous Mn increased
432 significantly (Figure 7). A field CO₂ injection (Kharaka et al., 2006) also showed aqueous Mn
433 increase, likely from Mn oxide dissolution.

Figure 5. Major aqueous ion concentrations in sandstone/brine/scCO₂ systems as a function of time and scCO₂ concentration: a) Ca²⁺; b) Mg²⁺, c) K⁺; d) CO₃²⁻; e) SO₄²⁻; f) Cl⁻. Symbols represent the initial brine (●), 10% scCO₂ (▲), 75% scCO₂ (◆), 90% scCO₂ (○), and 97% scCO₂ (■) in stop flow columns.

Figure 6. Minor aqueous ion concentrations in sandstone/brine/scCO₂ systems as a function of time and CO₂ concentration: a) silica, and b) Si/Al molar ratio. Symbols represent the initial brine (●), 10% scCO₂ (▲), 50% scCO₂ (▼), 75% scCO₂ (◆), 90% scCO₂ (● and ◆), and 97% scCO₂ (■) in stop flow columns.

Brine/scCO₂ fluid reacting with intact core showed an increase in some trace metals present as cations (Si, Fe, Ba, Mn, Sr, Ni, Sn, Bi, Cu, Li, P, and Zn) with the most significant increases in Si, Ni, Mn, B, and Sr (Figure 7), which is consistent with the hypothesized change in the acidic brine-scCO₂ environment. In the acidic environment created by the scCO₂, other studies have shown increased aqueous iron from iron oxides (Kharaka et al., 2009), and as described in Section 3.6, some of the 0.76% hematite in this sandstone is dissolving. Laboratory dissolution studies of three sandstones indicated that acidification from CO₂ introduction rapidly increased trace metals As, Ba, Cd, Fe, Mn, Pb, Sr, and U likely as a result of these trace metals in carbonates that were dissolved (Kirsch, 2013). Increased concentrations of other metals can be caused by dissolution of specific phases for Zn (ZnCO₃, Wang and Jaffe, 2004), Pb (PbS, Zheng et al., 2009) and As (arsenopyrite, Xu et al., 2010), although Pb and As solubility is low in the highly acidic water of these experiments. Trace metals observed to decrease in concentration included Co and Pb, and those below detection limits included As, Be, Cd, Mo, Se, Ag, Ti, U, and Zr. Metals present as oxyanions (Cr, As, Mo) were below detection limits in all systems (i.e., precipitated), which was also hypothesized to occur in the acidic environment. Metals that would be less mobile due to the presence of some O₂ in the scCO₂ (i.e., Fe, As) were below detection limits, but the Mn increased (Figure 7). Mercury is a volatile product of coal

464 combustion, so it is also found in scCO₂. In rock core/brine/scCO₂ experiments in which 688
465 µg/L Hg was added with other trace metals, ICP-MS showed that Hg decreased to below
466 detection limits (<12.5 µg/L). These experiments conducted at 20%, 50%, and 90% scCO₂
467 showed a weak correlation between scCO₂ concentration and trace metal concentrations with the
468 exception of Ni and Mn, which showed the highest concentrations at 20% scCO₂.

Figure 7. Trace aqueous metal concentrations in brine/scCO₂ systems as a function of time at a) 20% scCO₂, b) 50% scCO₂, and c) 90% scCO₂ (initial water shown at 10 h). Symbols represent

472 Ba (▲), Fe (▼), Al (◆), Si (●), Sr (◀), Hg (●), Bi (●), B (■), Co (◈), Cu (■), Pb (■), Li (▲),
473 Ni (●), Sn (◆), Zn (◈), and Mn (●).

474

475 3.4 Surface Phase Analysis of Cores

476 Comparison of untreated to scCO₂-treated cores showed changes in surface precipitates that were
477 correlated with changes in aqueous ion concentrations. For the untreated sandstone cores,
478 electron microprobe analysis of the untreated upper Mount Simon core at the 1204 m depth at a
479 resolution of 2 μm clearly shows the high concentration of silica (Figure 8b) and likely the
480 mullite aluminosilicate in the coarser grains. X-ray diffraction data indicated the presence of
481 1.8% mica, but could not distinguish among the three major micaceous minerals—muscovite
482 (KAl₂(AlSi₃O₁₀)(OH)₂), biotite (K(Mg,Fe)₃(AlSi₃O₁₀(OH)₂), and phlogopite
483 (KMg₃(AlSi₃O₁₀)(OH)₂). The aluminum concentration was higher in finer grained deposits
484 (Figure 8d). As suggested by the yellow-brown stains in the thin-section micrographs (Figure
485 1b), the highest Fe concentrations are in the finer grains (Figure 8e; porosity shown in Figure
486 8a). The spatial distribution of K is similar to that of Al (Figure 8f and d) and not that of Fe,
487 consistent with the presence of muscovite. Fe, thus, is likely present in non-micaceous minerals.
488 The Na distribution was mainly in large pores and not co-located with Cl (not shown), so likely
489 not NaCl.

Figure 8. Electron microprobe analysis of Mount Simon thin section showing a) electron backscatter image, b) Na, c) Si, d) Al, e) Fe, and f) K by elemental detection.

For cores subjected to 1.2 years of 98% scCO₂ and 2% brine, there were observed changes in surface precipitates that were correlated with the time scale of aqueous ion changes, but were too small to alter sandstone permeability. Solid phases identified in this treated sample were compared to solid-phase analysis conducted on untreated core. Brine is initially poorly displaced by the injecting scCO₂ in laboratory experiments representing near-injection-well conditions, even after 100 pore volumes of scCO₂ injection, likely due to the relatively short duration of the experiment not allowing for sufficient carbonate dissolution into aqueous solution. However, once a steady-state residual water content is achieved, slow partitioning of water into the scCO₂ (limited solubility) will continue to dewater the injection zone. As water partitions into the scCO₂, the remaining ions eventually become supersaturated and precipitate. This “salting-out” phenomenon has been observed by others working with NaCl precipitates (Gaus et al., 2008). Electron microprobe analysis of the scCO₂/brine-treated sandstone in this study shows extensive formation of small NaCl crystals on silica (Figure 9 a and b) and KCl crystals on silica (Figure 9c and d), which are likely the result of salting out. Aqueous measurements show that K⁺ (Figure 5c) and Na⁺ (not shown) actually increased over time and with a higher scCO₂ content. Other minor precipitate phases identified include an iron oxide, likely forsterite (or talc) on calcite (Figure 9 e and f), a Pb oxide precipitate (Figure 9 e and f), and BaSO₄ (Figure 9 g and h). Aqueous measurements showed that iron and lead concentrations decreased to below detection limits (Section 3.3). Aqueous iron may have decreased due to the oxidation caused by the planned O₂ present in the scCO₂ injection stream (Section 2.1).

Figure 9. Electron microprobe analysis of upper Mount Simon Sandstone treated with 98% scCO₂ and 2% brine at 12.41 MPa and 38°C for 1.2 years showing the formation of NaCl (a and b), KCl on quartz (c and d), forsterite and a lead oxide on calcite (e and f), and BaSO₄ (g and h). Images on the left are electron backscatter images and images on the right are elemental analysis of points shown in backscatter image.

3.5. Permeability and scCO₂ Injection

Because there was some mineral dissolution (i.e., based on changes in Mg²⁺, K⁺, Na⁺, and SO₄²⁻ concentrations, Figure 5) and minor precipitate formation (Figure 9), only minor changes in sandstone permeability was expected as a result of scCO₂ injection. However, the acidic scCO₂ also caused movement of iron oxide particles (Section 3.6), which could also influence permeability. Therefore, permeabilities of cores before and after different scCO₂ injection experiments were compared. Brine injections of intact cores prior to scCO₂ injection (upper Mount Simon, lower Mount Simon, Eau Claire Sandstones) were used to calculate porosity of all cores was 0.186 ± 0.0492 with an upper Mount Simon mean of 0.2009, a lower Mount Simon mean of 0.1804, and a Eau Claire mean of 0.1170 (Table 3). The average dry bulk density of the sandstones was 2.344 g/cm³ for the upper Mount Simon, 2.288 g/cm³ for the lower Mount Simon, and 2.487 g/cm³ for the Eau Claire. Based on pressure change during brine injection at four different velocities, the mean intrinsic permeability of the upper Mount Simon was 1.42×10^{-14} m², the lower Mount Simon was 8.11×10^{-15} m², and Eau Claire was 1.21×10^{-14} m². The anisotropy ratio of horizontal to vertical permeability was 0.22, 7.7, and 0.89 for three pairs of cores where both horizontal and vertical core subsamples were available. For a core in which 85 pore volumes of brine was injected (1204 m depth), there was some particulate mobilization (described in Section 3.6), but there was no significant change in the intrinsic permeability (Table 4). For a second core from the same depth, a total of 113 pore volumes of scCO₂ was injected, and brine-filled permeability measurements were made at selected intervals. The pressure measurements indicated a small, but statistically insignificant trend of increasing permeability, which may be caused by the removal of particulates (see following section).

Table 3. Measured intrinsic permeability of cores prior to scCO₂ injection.

Formation	depth (m)	core orientation	dry bulk density (g/cm ³)	porosity	k mean ± std. dev. (m ²)
upper Mt Simon	1202.9	vertical	2.391	0.1715	7.33 ± 1.84 E-14
	1203.9	vertical	2.393	0.2453	8.31 ± 0.30 E-15
	1203.9	vertical	2.390	0.1873	
	1202.9	vertical	2.390	0.2520	1.56 ± 0.41 E-14
	1203.9	vertical	2.389	0.1382	1.59 ± 0.07 E-15
	1203.9	vertical	2.306	0.1562	1.42 ± 0.18 E-15
	1198.4	horizontal	2.585	0.1722	1.05 ± 0.16 E-15
	1198.4	vertical	2.230	0.2148	4.67 ± 0.13 E-15
	1198.4	vertical	2.198	0.2008	1.82 ± 0.38 E-14
	1198.4	vertical	2.172	0.2709	4.03 ± 0.18 E-15
	1197.6	vertical		0.0982	
lower Mt Simon	1342.6	vertical	2.288	0.1521	1.87 ± 0.66 E-15
	1342.6	horizontal	2.288	0.2087	1.44 ± 0.21 E-14
Eau Claire SS	1183.9	vertical	2.545	0.1002	1.28 ± 0.07 E-14
	1183.9	horizontal	2.429	0.1338	1.14 ± 0.02 E-14

Table 4. Change in intrinsic permeability in an upper Mt Simon core (1204 m depth) with no end frits after brine or scCO₂ injection. The intrinsic permeability was measured using 100% brine.

fluid injected	pore volumes injected	k (m ²)
brine	0	5.97E-15
	4.6	5.03E-15
	14.9	6.18E-15
	84.7	6.36E-15
scCO ₂	0	6.55E-15
	5.4	7.16E-15
	15.8	7.72E-15
	112.8	8.65E-15

3.6. Particulate Mobilization

The mobilization of iron oxide particles from the upper Mount Simon Sandstone core due to injection of scCO₂ was investigated because of its potential to change formation permeability and the influence on geochemical reactions. Particulate mobilization of clays in a sandstone aquifer was hypothesized to occur due to high mechanical forces near an injection well during scCO₂ injection (Lu et al., 2011). The acidification of formation materials caused by contact with scCO₂ results in dissolution of some of the ferric oxides (i.e., the 0.76% hematite), which may precipitate down gradient. In addition, dissolution could result in the movement of hematite particulates/colloids, potentially clogging down gradient pores. Experiments were conducted

using varying amounts of acidification (i.e., higher scCO_2 /brine ratio results in a lower pH), a range of reaction times, and different injection fluids (i.e., brine or scCO_2) to evaluate the total particulate mass moving down gradient.

Sandstone cores reacted with specific scCO_2 /brine solutions for 500 h showed that increasing the fraction of scCO_2 in the core increased the solids mobilization (Figure 10a). Additional experiments were conducted in which the fractions of solids mobilized by brine injection versus scCO_2 injection were compared over time as either brine or scCO_2 was injected (Figure 10b). Injecting scCO_2 mobilized significant amounts of iron oxide particulates (or mobilized aqueous iron that subsequently precipitated); e.g., 50 mg/g core after 1.5 pore volumes, 60 mg/g core after 10 pore volumes, and 180 mg/g after 100 pore volumes (cumulative solids mass, red data in Figure 10b). It should be noted that injection of 100 pore volumes of scCO_2 took 10 h to complete, which increases the reaction time for carbonate to partition from the scCO_2 into the brine when compared with smaller pore volume injections. One likely experimental artifact is that these 2.54 cm diameter cores have some loose iron oxide coatings at the outer edge of the drilled core. Injection of brine into brine-filled cores (i.e., no contact with scCO_2 ; black triangles in Figure 5b) showed some particulate movement after 1 pore volume (~45 mg/g), which increased only slightly after 100 pore volumes (~65 mg/g). Because this is considered background particulate movement, a realistic mass of iron oxide particulate movement from the injection of scCO_2 is the total observed minus this background value (i.e., 10 mg/g after 1 pore volume, 30 mg/g after 10 pore volumes, and 115 mg/g after 100 pore volumes of injected scCO_2). Although there was evidence of particulate movement observed in these 1D columns (i.e., linear flow systems), it is likely that this effect would be less significant at the field scale because of the radial flow system associated with well injection. Any particulate movement near the injection well would advect particles into an ever-increasing volume further away from the injection well, so this effect would likely to have less impact on field-scale intrinsic permeability than was measured in this laboratory study.

Figure 10. Transport of particulates from the upper Mount Simon Sandstone core material with a) 500 h reaction time at differing brine/scCO₂ mixtures, and b) variable reaction time (0.3 pore volume/minute) and brine (triangles) or scCO₂ (diamonds) injection. In (a), symbols represent 100% brine/0% scCO₂ (▲), 10% scCO₂ (▼), 30% scCO₂ (▵), 50% scCO₂ (▹), 70% scCO₂ (◆), 90% scCO₂ (◆), 95% scCO₂ (●), 98% scCO₂ (◻), and 100% scCO₂ (◼). In (b), black triangles represent experiments with 100% brine injection and red diamonds 100% scCO₂ injection.

3.7 Anaerobic and Aerobic Microbial Growth with scCO₂ Injection

Microbial activity observed under scCO₂ conditions (Peet et al., 2015) could influence permeability only if there was significant growth. In addition, significant microbial activity could also the rate of calcite dissolution (Luttge and Conrad, 2004). Therefore, microbial biomass growth was evaluated in differing scCO₂/brine fractions in high pressure no flow reactors over 100s to 1000s of hours. The microbial biomass measured in the untreated Mount Simon Sandstone at the 1197 m depth was $4.02 \pm 4.01 \times 10^5$ cells/g ($n = 10$, Table 5). This value is within the range previously reported for marine deposited sediments. In a study of sandstone and shale marine deposits in New Mexico from the late Cretaceous period (120-135 Myr) at a 450 to 750 ft depth, or similar depositional environment to the Mt Simon sandstone and Eau Claire shale, microbial biomass averaged 3×10^7 to 2×10^8 cells/g (Ringelberg et al., 1997), using a conversion of 20,000 to 30,000 cells/pmol of PLFA (Green and Scow, 1999, Zink et al., 2008). For comparison, as the Mt Simon sandstone was marine depositional environment, current sediments from deep Pacific ocean cores (12,000 ft water depth, 150' to 300' depth into sediment) averaged 10^6 to 10^7 cells/g, with ocean floor sediments (i.e., at the sediment/water interface) averaged 10^8 cells/g (Inagaki et al., 2006).

To demonstrate that the cells are viable, a second sample of brine included a microbial growth medium, which contained electron acceptors, trace metals, vitamins, and amino acids. This medium addition resulted in significant growth (540x) in 770 h to a cell count of $2.16 \pm 0.05 \times 10^8$ cells/g (Table 5). No attempt was made to evaluate which nutrients the cells were lacking, but this demonstrates that if the limiting nutrients are added to this deep subsurface microbial population, significant growth can occur.

The observed anaerobic microbial growth by 770 h correlated with higher scCO₂ concentration only (i.e., no additional trace metals; Table 5). Only two CO₂ saturations were evaluated, 50% and 98% scCO₂, which showed $1.71 \pm 1.08 \times 10^6$ (4.2 times growth, 50% scCO₂) and $4.49 \pm 0.62 \times 10^6$ cells/g (11.2 times growth, 98% scCO₂). Geochemical experiments show the pH has decreased to 6.3 (50% scCO₂) or 5.2 (97% scCO₂, Figure 4), with significant increase in K⁺, CO₃²⁻, SO₄²⁻ (Figure 5). With the addition of trace metals, anaerobic growth as a function of the fraction of scCO₂ was slightly less (i.e., 7.6 times growth by 770 h at 98% scCO₂). Most trace metals under these more acidic conditions remain aqueous (Figure 7) and bioavailable. Proof that this observed microbial growth is likely caused by methanogenesis would require measurements of the consumption of the CO₂ or production of methane.

Anaerobic growth measured as a function of time in a system in which only 90% scCO₂ (no trace nutrients) was added showed slow growth, peaking at 1300 h ($9.39 \pm 4.07 \times 10^6$ cells/g) the untreated biomass, then a slight decrease by 2200 h ($6.94 \pm 4.07 \times 10^6$ cells/g). Changes in major ions concentrations occurred at a similar time scale (100s of hours), with few additional change at longer time periods to 10,000 h (Figure 5). The effect of scCO₂ on anaerobic microbial growth effect could be indirect. Microbial growth is previously reported as a function of the fraction of CO₂ (Dixon and Kell, 1989, Peet, 2015). Injection of scCO₂ acidifies the system and desorbs heavy metals from clay, iron oxide, and other mineral surfaces, and also causes some dissolution of ferric oxides. Trace metals were shown to remain in aqueous solution (Figure 7). Trace metals may, therefore, be more bioavailable and promote more rapid microbial growth (i.e., used in microbial enzymatic pathways). In addition, ferric iron is used as an electron acceptor by iron-reducing microbes, so dissolution of ferric oxides may increase electron acceptor bioavailability.

Table 5. Microbial biomass in untreated and scCO₂/brine-treated Mt Simon Sandstone cores.

conditions/additions	scCO₂ (%)	time (h)	cell counts (cells/g)	treated/untreated
none	0	0	4.02 ± 4.01 E5	1.00
anaerobic	50	768	1.71 ± 1.08 E6	4.25
	98	768	4.49 ± 6.19 E6	11.2
anaerobic w/trace metals	10	768	3.34 ± 2.18 E5	0.83
	50	768	3.97 ± 2.14 E5	0.98
	98	768	3.06 ± 3.06 E6	7.61
anaerobic	90	16.3	2.02 ± 1.46 E6	5.04
	90	71.1	2.30 ± 1.37 E6	5.71
	90	364	2.48 ± 1.90 E6	6.18
	90	430	3.02 ± 1.81 E6	7.52
	90	598	4.49 ± 6.19 E6	4.20
	90	768	4.49 ± 6.19 E6	11.2
	90	1293	9.39 ± 4.07 E6	23.4
	90	2211	6.94 ± 4.47 E6	17.3
aerobic w/O ₂ , NO _x , SO _x	90	16.3	1.61 ± 1.22 E6	4.00
	90	71.1	1.37 ± 6.94 E5	3.42
	90	364	1.13 ± 1.29 E6	2.81
	90	430	1.31 ± 9.37 E5	3.26
	90	598	2.17 ± 1.21 E6	5.40
	90	768	3.36 ± 4.74 E6	8.35
	90	1293	5.64 ± 3.05 E6	14.0
	90	2211	3.76 ± 2.94 E6	9.36
aerobic w/O ₂ , NO _x , SO _x , PO ₄ , amino acids	90	768	2.16 ± 0.05 E8	538.0

Near the injection well, the mass of injected oxygen would eventually overwhelm the reductive capacity of the aquifer (ferrous iron in aqueous solution and any reduced Fe or Mn surface phases), so oxic microbial growth was also investigated. The presence of oxygen would actually inhibit methanogenesis. In general, aerobic microbial growth with trace-gas components (SO_x, NO_x) was less than anaerobic microbial growth at all time periods (Table 5). After 500 h, aerobic microbial growth was only 3.3 times. It increased to 14 times after 1300 h and leveled off thereafter.

Overall, the maximum of 23.5 times growth relative to untreated sandstone observed by 1300 h (anaerobic case) was minor and would have no influence on permeability in the Mount Simon Sandstone. While microbial growth in these no-flow laboratory experiments indicate some microbial growth is likely at field scale, experiments cannot be used to predict the amount of growth near an injection well. Measured aerobic microbial biomass growth after 1300 h in scCO₂/brine/Mount Simon core systems was 14 times ($5.64 \pm 3.05 \times 10^6$ cells/g) that of the untreated biomass. Given an average cell density of 2.8×10^{-13} g/cell (Bailey and Ollis, 1986), the untreated biomass is 1.1×10^{-7} g cells/g sandstone, and would occupy approximately 0.004%

of the pore space (assuming 17% porosity; Cunningham and Characklis, 1991). The maximum observed biomass increase in a field-realistic system ($9.39 \pm 4.07 \times 10^6$ cells/g in an anaerobic system) would occupy 0.09% of the pore space, which is a significant increase, but still too small to influence permeability (Cunningham and Characklis, 1991). With a continuous influx of microbial nutrients, biomass could potentially continue to increase, near the injection well, so nutrients would generally not be transported down gradient (i.e., no down gradient growth [Taylor and Jaffe, 1990]). In addition, microbes generally attach to mineral surfaces by a variety of mechanisms, but can be sheared off with high velocities and high-ionic-strength solutions. As microbes occupy a substantial fraction of the pore space, fluids traveling through the remaining pore space will be moving at a higher velocity, which eventually exceeds the microbe-surface attachment strength and additional growth at that location does not occur (Cunningham and Characklis, 1991). Although microbial growth was small in this study, because microbial activity can inhibit the rate of calcite dissolution (Luttge and Conrad, 2004, Warren et al., 2001), and can control rates of mineral weathering (Park et al., 2009), further investigation of the influence of microbial activity on the sandstone-brine-scCO₂ system is needed.

4.0 Summary and Implications

Laboratory experiments were conducted to evaluate the impact of scCO₂ injection on aqueous and solid phase geochemistry of the brine-filled sandstone, and secondary effects of permeability changes caused by precipitates, particulate movement, or microbial growth. In addition, changes in trace metals were evaluated due to the potential impact on water quality if injection aquifer fluids leaked into overlying formations. Experiments showed that low viscosity scCO₂ displacement of the brine is inefficient by advection, as scCO₂ travels predominantly in larger pores, leaving significant brine in smaller pores. After 10 pore volumes of scCO₂ injection, scCO₂ saturations were 25 to 40%, and after 100 pore volumes of injection, scCO₂ saturations had only reached 50 to 65%. In contrast, brine displacement of the scCO₂-filled core was more rapid; brine saturations reached 45 to 70% after 10 pore volumes of brine injection. The incomplete mixing and multiphase nature of the scCO₂/brine fluids likely slowed fluid interactions with the sandstone. The scCO₂ injection experiments also showed a moderate amount of particulate (iron oxides) transport, which was correlated with the fraction of scCO₂

684 injected. However, the sandstone permeability did not change even after injecting 115 pore
685 volumes of scCO₂ or brine, in spite of particulate movement. Long-term (1.2 years) major
686 geochemical changes observed include: 1) significant increase in Mg²⁺, K⁺, and SO₄²⁻ (10s to
687 100s of mmol/L), 2) dissolution of the hematite coating on the quartz grains, and 3) precipitation
688 of NaCl and KCl. Trace metals present as cations observed to increase during scCO₂ injection
689 (i.e., acidification) include silica, Ba, Mn, Sr, Ni, Sn, Bi, Cu, Li, P, and Zn, as predicted. Trace
690 metals present as oxyanions (As, Mo, Cr) were observed to decrease, as predicted. Trace metals
691 Hg, Pb, and Co showed a decrease. The increase in Mg²⁺, K⁺, Na⁺, SO₄²⁻, silica, and Al³⁺
692 concentrations were greatest with highest scCO₂/brine ratio (i.e., more acidic) are likely caused
693 by the rapid carbonate and hematite dissolution (hours), then clay dissolution (100s of hours),
694 then albite and K-feldspar dissolution (1000s of hours). As the system neutralizes, minerals
695 expected to precipitate include dolomite, diasporite, hematite, and quartz. Metals that should be
696 less mobile in the presence of O₂ in the scCO₂ (i.e., Fe, As) decreased, but Mn increased. These
697 increases were rapid (< 100 h), and indicative of desorption or rapid dissolution. Electron
698 microprobe analysis of the sandstone after year-long experiments showed the precipitation of
699 some NaCl, KCl, and minor amounts of a lead oxide, and forsterite, but of insufficient mass to
700 significantly change the intrinsic permeability. The microbial biomass measured in the untreated
701 Mount Simon Sandstone at the 1197 m depth was $4.02 \pm 4.01 \times 10^5$ cells/g was within the range
702 previously reported for marine deposited sediments. Some anaerobic and aerobic microbial
703 growth was observed (23 and 14 times, respectively) that was correlated with higher scCO₂
704 concentration. The observed microbial growth observed would likely have no influence on
705 permeability in the Mount Simon Sandstone, because the calculated change in pore space
706 occupied by increase in microbial biomass is insignificant. The small observed geochemical and
707 microbial changes are not expected to reduce the ability to inject scCO₂ into the reservoir, but
708 significant increases in trace metal concentrations could magnify the impact of a potential leak of
709 reservoir fluids into an overlying aquifer.

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