Numerical simulation of porosity and permeability evolution of Mount Simon sandstone under geological carbon sequestration conditions

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Abstract

A numerical model was developed with the use of reactive transport code CrunchFlow to estimate porosity, permeability and mineral composition changes of Mount Simon sandstone under typical geological carbon sequestration conditions ($P=23.8$ MPa and $T=85$ °C). The model predicted a permeability decrease from 1.60 mD to 1.02 mD for the Mount Simon sandstone sample in a static batch reactor after 180 days of exposure to CO₂-saturated brine, which is consistent with measured permeability results. Model-predicted solution chemistry results were also consistent with laboratory-measured solution chemistry data. SiO₂ (am) was the primary mineral that causes permeability decrease, followed by kaolinite. Both SiO₂ (am) formation and kaolinite formation were attributed to the dissolution of quartz and feldspar. This study shows that the formation of SiO₂ (am) and kaolinite in the pore space of host rock is possible under typical CO₂ sequestration conditions. SiO₂ (am) and kaolinite precipitation at the CO₂ plume extent could reduce the permeability of host rock and improve lateral containment of free-phase CO₂, contributing to overall security of CO₂ storage.

Key words: CO₂ sequestration; sandstone formation; reactive transport model; permeability; porosity

1. Introduction

Carbon capture and sequestration (CCS), which involves capture of large quantities of carbon dioxide from flue gas and injecting carbon dioxide into permeable geological formations at depth (Gasda et al., 2008) sufficient to ensure safe long-term storage, is a promising strategy to reduce the emissions of greenhouse gas to the atmosphere. Projections by the Global CCS Institute (2011) suggest that CCS would need to account for 19 % of total CO₂ emission reduction to reach the CO₂ emission target by 2050. Deep saline aquifers have been reported to have the highest estimated CO₂ storage capacity of all candidate geologic storage targets - at least 1738 Gigatonnes of CO₂ in North America alone (The North American Carbon Storage Atlas, 2012). The interaction between injected CO₂ and host rock in deep saline aquifers for CO₂ sequestration is of interest because a) the interaction between injected CO₂ and host rock may result in porosity and permeability changes of host rock, which would directly impact CO₂ storage capacity, CO₂ plume migration, and reservoir pressure response; b) the interaction between injected CO₂ and host rock may result in permanent storage of some of injected CO₂ as carbonate minerals, and could potentially release unwanted ions (e.g., arsenic from arsenopyrite in host rock, Parthasarathy et al., 2011) to the aquifers.

There is a wide range of pressure and temperature for CO₂ sequestration conditions. The pressure can range from 7.3 MPa to 65 MPa and the temperature can range from 31°C to 132 °C. In this study, the CO₂ sequestration conditions are defined as a pressure of 23.8 MPa and a temperature

of 85 °C, which correspond to a formation depth of around 2.4 km given a pressure gradient of 10^4 Pa/m.

There have been a number of experimental studies that investigated the physical and chemical property changes of host CO₂ storage rock when exposed to CO₂ (Luquot and Gouze, 2009; Fu et al., 2009; Morris et al., 2009; Lu et al., 2011; Liu et al., 2012; Luquot et al., 2012; Carroll et al., 2012; Karamalidis et al., 2012; Soong et al., 2014). Important conclusions that can be derived from those previous studies are: a) the nature of physical and chemical changes of host rock is dependent on its mineral composition, and on the progressive dissolution of CO₂ that results in a decrease of pH in brine (Luquot and Gouze, 2009). b) CO₂-sandstone interaction usually does not result in formation of CaCO₃ within short exposure period (Carroll et al., 2012; Soong et al., 2014), but slow dissolution of feldspar minerals would cause CaCO₃ to ultimately precipitate (Kharaka et al., 2013). More carbonate minerals would ultimately precipitate from sandstones that have abundant feldspar minerals and where the feldspars are more calcic (Kharaka et al., 2013). c) dissolution of feldspar in feldspar-rich host rock usually results in precipitation of secondary clay minerals (e.g., montmorillinite and kaolinite) (Fu et al., 2009; Liu et al., 2012; Carroll et al., 2012); and precipitation of secondary clay minerals can offset porosity and permeability changes as a result of feldspar dissolution (Soong et al., 2014).

Results from experimental studies help researchers identify key geochemical reactions and enable insights into reaction pathways of host rock–CO₂ interaction under CO₂ sequestration conditions. Results from experimental studies also help develop and constrain geochemical models. However, experimental studies have limitations. First, they are limited to relatively short

time scales (typically days to months), and it is difficult to predict long-term physical and chemical property changes of host rock (e.g., 30–1000 years) under CO₂ sequestration conditions. Second, rigorous experimental exploration of parameter space for controlling variables, such as initial porosity of host rock, feldspar wt% of host rock and aqueous CO₂ concentration after CO₂ injection, are time-consuming, expensive and sometimes not feasible in the laboratory. Computer-based reactive transport modeling overcomes these limitations, enabling extrapolation of findings from relatively short experiments to longer time scales and parameter sensitivity analyses (Gunter et al., 1997; Gaus et al., 2005; Johnson et al., 2005; Xu et al., 2011; Gherardi et al., 2012). There have been some studies that focused on modeling of interactions between CO₂-saturated brine and reservoir host rock (or caprock). Johnson et al. (2005) used a reactive transport model to assess the evolution of caprock permeability due to CO₂ injection-induced mineral alteration. Zerai et al. (2006) conducted equilibrium, path-of-reaction and kinetic modeling of CO₂–brine–mineral reactions in the Rose Run Sandstone in Ohio to investigate the factors that are likely to influence the capacity of this formation to trap injected CO₂. Xu et al. (2011) applied a generic two-dimensional (2-D) radial TOUGHREACT model to illustrate the temporal evolution and spatial distribution of the injected CO₂ and the subsequent physical and chemical changes of the reservoir host rock under CO₂ sequestration conditions. Liu et al. (2011) performed numerical simulation of large scale CO₂ injection (a million tons per year for 100 years) into Mount Simon sandstone. Gherardi et al. (2012) also applied TOUGHREACT code to predict mineral alteration in both the cement of an idealized abandoned wellbore and the caprock adjacent to the wellbore at the top of a potential CO₂ storage aquifer (Dogger aquifer) in Paris Basin, France.

Most reactive transport models to study the interaction between host rock and CO₂-saturated brine rely on kinetic and equilibrium constants that are uncertain (or maybe even unreliable). So it is prudent to compare modeling results with experimental results to help understand the implications of model predictions, and to explore sensitivity of model results to reasonable perturbation of those key parameters. One study investigated the mineral composition change of Mount Simon sandstone samples after exposure to CO₂-saturated brine with the use of reactive transport modeling, and the mineral composition results from modeling were compared with experimental data (Carroll et al., 2012). However, more studies are needed to compare modeling results with experimental data.

In this study, a numerical model that is able to simulate porosity, permeability and mineral composition changes of host rock under CO₂ storage conditions is presented. The model is compared with experimental results (permeability and solution chemistry data) from Soong et al. (2014). Both the model and the experimental study done by Soong et al. (2014) are representative of the post CO₂ injection period where the CO₂ plume is stabilized and the system pressure returns to pre-injection values. In the experiment of Soong et al., one cylindrical sandstone sample (2.54 cm in diameter × 5.08 cm in length) obtained from a depth of 1,769.7 m from a well located in Vermillion County, IN was exposed to CO₂-saturated brine ($P(\text{CO}_2) = 23.8\text{MPa}$ and temperature = 85°C) in a static (no flow) high pressure vessel with a Teflon liner. The exposure time was 180 days. The initial brine composition in the experiment of Soong et al. (2014) is shown in Table 1. An equilibrium calculation based on initial brine composition and exposure conditions was performed using CrunchFlow to take into account potential mineral super-saturation at elevated temperature under given exposure conditions. The brine composition

after equilibrium calculation is reported in Table 1. Despite significant concentration decrease for Ba^{2+} , H_4SiO_4 (aq) and Al^{3+} shown in Table 1, CrunchFlow does not predict any mineral precipitation when the system reaches equilibrium, which implies that minerals that have potential to precipitate (i.e., BaSO_4 and $\text{K}_{0.85}\text{Al}_{2.85}\text{Si}_{3.15}\text{O}_{10}(\text{OH})_2$) have not reached super-saturated state. Therefore, the sandstone porosity change after 180 days of exposure is caused by interaction between sandstone and brine, not precipitation of minerals from super-saturated brine. More details about the experiment can be found in Soong et al. (2014).

Most previous studies are focused on the reaction pathways for interaction between host rock and CO_2 -saturated brine, while the correlation between chemical reactions and change in porosity and permeability has not been extensively studied. This study demonstrates a methodology to couple reactive transport modeling and permeability evolution modeling, and the results from this study provide a link between chemical reaction and permeability change. A comprehensive sensitivity analysis is conducted to investigate how the changes of important modeling parameters affect permeability evolution, which has not been reported in previous studies. Though the simulations performed in this study are not field scale, the results from this study can be used to demonstrate how chemical reactions might affect the permeability of Mount Simon formation after injection of CO_2 .

2. Model description

2.1 Model set up

A 1-D reactive transport model was developed with the use of the multicomponent reactive transport modeling code CrunchFlow (Steefel, 2009). The model simulates interactions between

CO₂-saturated brine and a Mount Simon sandstone sample, and yields mineral composition and porosity changes of the sample. The model is focused on the post injection period, and the simulations performed were able to capture the conditions at locations close to the CO₂ plume after injection of CO₂ (i.e., near-static (no flow) condition, pressure is close to pre-injection reservoir pressure, and brine is saturated with CO₂). Two scenarios with different simulation durations were tested. The first scenario had a modeled reaction time of 180 days, which was the same as the exposure time of the sandstone exposure experiment (Soong et al., 2014); the second scenario had a modeled reaction time of 30 years, which was selected to explore permeability and porosity changes of the sandstone sample after very long exposure time.

A schematic of the modeling region is illustrated in Figure 1. In the 1-D model, the sandstone sample is divided into 1,000 grid blocks and each block has a length of 2.54×10^{-3} cm. The ratio of the brine domain width (296 mm) to sandstone domain width (25.4 mm) equals to the ratio of brine volume to sandstone volume in the high pressure vessel, so as to accurately model solution chemistry. The model is a closed boundary model with no flow, which mimics the conditions in the high pressure vessel. The model requires inputs of equilibrium constants and rate constants for dissolution and precipitation reactions of minerals, which yields volume fraction changes of minerals at each grid block. Key model input parameters are discussed in Section 2.4. Change of porosity at each grid block is correlated with volume fraction changes of minerals by equation (1):

$$\phi(t) = 1 - \sum_{i=1}^m fr_i(t) - fr_n \quad (1)$$

where,

161 $\phi(t)$ is the porosity at time t , $fr_i(t)$ is the volume fraction of reactive mineral phase i at time t and
 162 fr_n is the volume fraction of all inert mineral phases. In this study, all mineral phases involved
 163 are active and there are no inert phases. The initial porosity of the sample ($\phi(t = 0)$) is equal to
 164 7.9%, and the porosity was measured using a helium porosimeter (HP-41, Temco, Inc) at 0.7
 165 MPa and ambient temperature (Soong et al., 2014).

166

167 The volume fraction of each mineral can be calculated with the use of mineral molar fraction and
 168 the molar volume of each mineral:

$$fr_i(t) = \frac{Mol_i(t) \times V_{molar-i}}{\sum_{i=1}^n Mol_i(t) \times V_{molar-i}} \quad (2)$$

169 where,

170 $Mol_i(t)$ is molar fraction of mineral i at time t and $V_{molar-i}$ is molar volume of mineral i . Molar
 171 volumes of all minerals are listed in Table 2.

172

173 CrunchFlow uses the law of transition state theory (TST) to calculate mineral precipitation and
 174 dissolution rates. The simplified expression of the mineral dissolution/precipitation rate law can
 175 be written as (Steefel, 2009):

176

$$R_{ir} = A \left(\sum_{l=1}^M k_l \left(\prod_{i=1}^N a_i^{p_i} \right) \left(1 - \frac{Q}{K_{eq}} \right) \right) \quad (3)$$

177 where,

A is the specific surface area of the mineral involved in the reaction, k_l is the l^{th} parallel reaction rate constant that contributes to the dissolution/precipitation of the mineral, $\prod_{i=1}^N a_i^{\text{pi}}$ describes the effects of various ions in solution on the dissolution/precipitation rate of parallel reaction l , Q is ion activity product (*e.g.*, for reaction $aA + bB \leftrightarrow cC + dD$, Q is equal to $\frac{[C]^c[D]^d}{[A]^a[B]^b}$), and K_{eq} is equilibrium constant of the reaction. The ratio of Q to K_{eq} (Q/K_{eq}) determines the direction of the reaction. For example, given calcite dissolution reaction $\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$, if Q is higher than K_{eq} , then the system is supersaturated with Ca^{2+} and HCO_3^- , and the reaction will proceed in the direction of calcite precipitation. Rate constants and $\prod_{i=1}^N a_i^{\text{pi}}$ values used in this study are described in Section 2.4.

2.2 Solution chemistry modeling

The dissolution and precipitation of minerals result in concentration changes of cations and anions within the pore space of the sandstone, and the cations and anions released to the pore space will migrate to bulk brine driven by diffusive transport. In this study, the concentrations of major elements in bulk brine (*i.e.*, Ca, Na, Mg, K, Fe and Si) after 180 days of exposure were modeled and the modeled concentrations were compared with concentrations measured by Soong et al. (2014) to make sure that the model captures key mineral dissolution and precipitation processes. In Soong et al. (2014), brine solution from the high-pressure vessel was filtered, acidified and diluted, and then analyzed with the use of a Dionex DX-100 ion chromatograph equipped with a conductivity detector (Dionex, Inc. – Sunnyvale, CA, USA) (Soong et al., 2014) to determine major element concentrations. The concentrations were only measured at the end of the exposure experiment (*i.e.*, $t=180$ days).

2.3 Permeability modeling

The permeability change of each grid block can be correlated with porosity change with the use of the following equation (Brunet et al., 2013; Zhang et al., 2013).

$$\frac{perm_{i,t}}{perm_{i,0}} = \left(\frac{\phi_{i,t}}{\phi_{i,0}}\right)^n \quad (4)$$

where $perm_{i,t}$ is the local permeability in the block i at time t ; $perm_{i,0}$ is the initial permeability in the block i (1.6 mD for every block); $\phi_{i,t}$ is the porosity in the block i at time t ; $\phi_{i,0}$ is the initial porosity in the block i . Hereby the initial porosity at each grid block is assumed to be equal to the initial porosity of the entire sample (7.9%), because the helium porosimeter method used by Soong et al. for porosity measurement can only yield the porosity of the entire sample, and the method does not provide characterization of porosity distribution of the sample. Therefore, the initial porosity at each grid block cannot be specified. n is an exponential coefficient, which is set to be 11. The large n value is suggested by Brunet et al. (2013) and is consistent with observations and quantification for porosity–permeability evolution induced by chemical reactions (Brunet et al., 2013).

The correlation between the overall permeability and the permeability of each block can be written as (Craft et al., 1991):

$$perm_{v,t} = \frac{\sum_{i=1}^n h_i perm_{i,t}}{L} \quad (5)$$

where $perm_{v,t}$ is the vertical permeability at time t ; L is the width of the sample (2.54 cm); h_i is the width of the individual block (2.54×10^{-3} cm); $perm_{i,t}$ is the local permeability in the block i at time t , and n is the total number of blocks (1,000).

Compared with complicated permeability calculation models such as Bautista–Manero–Puig (BMP) model (Turcio et al., 2013) and lattice Boltzmann (LB) model (White et al., 2006), this simple permeability model is easy to use and is sufficient for permeability calculation given known initial permeability and porosity.

The modeled vertical permeability after 180 days of exposure ($perm_{v,180}$) was compared with laboratory-measured vertical permeability of the sample. An Autolab 1500 unit from New England Research, Inc. was implemented for permeability measurements. The central part of the Autolab 1500 apparatus is a high pressure chamber, where confining pressure is created to simulate underground conditions. A porous core sample is secured in a core holder and placed inside the pressure chamber. A pressure transient method was used for permeability measurements. During every individual measurement, the confining pressure was maintained at a constant value (42 MPa) to simulate actual field conditions. A pressure pulse was introduced at the upstream side, and the pressure at the downstream side was recorded. Based on the observed downstream pressure pulse, the permeability of the core sample was determined. During the measurement, the sample was held for several hours under continuous nitrogen “flow through” at the rates of about 0.1–0.2 mL/sec. More details of permeability measurement can be found in Soong et al. (2014). It is important to note that no subcores were taken across the core to capture the permeability of different zones.

In the batch reactor, the reactions are governed by diffusion, not permeability. However, reactions driven by diffusion cause dissolution and precipitation of minerals, which result in

permeability change of the sample. Therefore, permeability change is a result of diffusion-driven reactions and the permeability change does not affect reactions in the batch reactor.

2.4 Important modeling parameters

Based on the CO₂ solubility model developed by Duan and Sun (Duan and Sun, 2003), the concentration of dissolved CO₂ in brine under given exposure conditions was 0.689 mol/kg, partial pressure of CO₂ (discounting for water vapor) was 237.4 bar, and fugacity of CO₂ was 122.9 bar. The fugacity of CO₂ equals to fugacity coefficient of CO₂ × CO₂ partial pressure. Fugacity coefficient of CO₂ is from a look-up table based on the equation of state in Duan et al. (2003), and the equation of state is described in SI. Based on CrunchFlow calculation, the brine pH was 4.13, given a dissolved CO₂ concentration of 0.689 mol/kg. The effective diffusivity exponent (m) was 2.0. m is used to calculate effective diffusivity in porous media from molecular diffusivity. The correlation between effective diffusivity and molecular diffusivity is:

$$D_e = D_0 \Phi^m \quad (6)$$

where D_e is effective diffusivity, D_0 is molecular diffusivity (a property of the diffusing specie), Φ is porosity of the rock matrix, and m is the effective diffusivity exponent of the rock matrix. The exponent m varies between 1.3 and 2.0 for brine-saturated rocks (Bruggeman, 1935; Archie, 1942; Adler et al., 1992; Grathwohl, 1992; Shimamura, 1992). In this study, an m value of 2.0 is chosen, which produces permeability result that is consistent with laboratory-measured permeability (see SI for details).

Table 2 shows the mineral composition of the unreacted Mount Simon sandstone, and Table 3 shows equilibrium constants of the reactions involved in the model, and reaction rate constants

and $\prod_{i=1}^N a_i^{P_i}$ values that are used for the model. Specific surface areas and molar volumes of minerals involved in the model can be found in Table 2. It is important to note that there is no calcite in unreacted Mount Simon sandstone sample to buffer the pH.

2.5 Sensitivity analysis

A sensitivity analysis was conducted to assess how changes of the modeling parameters affect the simulation results. Seven modeling parameters (i.e., initial concentration of dissolved CO₂, initial porosity of the sandstone, total feldspar content of the sandstone, annite content of the sandstone, equilibrium constant of SiO₂ (am) precipitation reaction, precipitation rate constant of SiO₂ (am), and exponent (n) in equation 4) were tested. Values tested for each parameter and the justification to test each parameter can be found in Table 4. For each analysis, only one variable was varied from the initial conditions, and all the other variables were maintained the same as the initial conditions.

3. Results

3.1 Solution chemistry, porosity, pH and mineral composition results

Table 5 shows a comparison between model-predicted major element concentrations and laboratory-measured major element concentrations after 180 days of exposure. The concentrations predicted by the model are consistent with measured concentrations.

Figure 2 shows the changes of porosity, pH and volume % of minerals as a function of the distance away from the external sandstone surface in contact with bulk brine after 180 days of exposure. The porosity of the sandstone in the region close to the surface (Figure 2a) increased with the increase of exposure time, which is mainly attributed to the dissolution of feldspar

(Figure 2c) and quartz (Figure 2d). The porosity of the sandstone in the region next to the high-porosity region decreased with the increase of exposure time, which is primarily attributed to the precipitation of SiO_2 (am) (Figure 2j). Precipitation of other minerals (i.e., kaolinite and muscovite/illite) also contributed to the decrease of porosity in this low-porosity region (Figures 2f and 2i). Small amount of siderite (less than 0.07%, see Figure 2g) was predicted to form in the region more than 4 mm away from the sandstone surface. The very small amount of siderite formed did not contribute much to porosity decrease. After 180 days of exposure, the pH at the surface of the sample was 4.20 and the interior of the sample (5 mm from the sample surface) had a pH of 4.38. Both pH values were higher than the pH of bulk brine. That is to say, the sandstone sample had moderate pH buffering capacity, which can be attributed to presence of feldspar in the unreacted rock matrix. As for secondary clay mineral formation, the main clay mineral formed was kaolinite. In summary, dissolution of feldspar is the key reaction to cause porosity decrease in the sandstone sample, because the dissolution of feldspar results in release of Al^{3+} (aq) and SiO_2 (aq), which cause precipitation of SiO_2 (am) and kaolinite.

3.2 Permeability results

Figure 2a shows that the sandstone sample exposed to CO_2 -saturated brine for 180 days had a high-porosity zone adjacent to the surface of the sample in contact with bulk brine, and the zone next to the high-porosity zone had much lower porosity. Results in Figure 2 implies that there is a low-porosity and low permeability zone at the edge of the sandstone sample after exposure to CO_2 -saturated brine, and there is a location that has the lowest porosity and lowest vertical permeability in the low-porosity zone (see Supporting Information for details). In permeability calculation, the vertical permeability of that location is approximately the vertical permeability of the entire sample, because the vertical permeability of the entire sample is determined by the

zone with the lowest vertical permeability. A schematic of vertical permeability calculation as permeability of each sample interval in series is shown in Supporting Information.

Figure 3a shows the distribution of porosity in the lowest-permeability location, which represents the permeability of the entire sample. Based on Figure 3a and equations (4) and (5), the overall permeability of this location (approximately the same as the vertical permeability of the entire sample) was calculated. Figure 3b shows permeability change of the Mount Simon sandstone sample exposed to CO₂-saturated brine for 180 days. Both experimental results (obtained from Soong et al. (2014)) and model simulation results are reported in Figure 3b. The model predicted a decrease of permeability (from 1.60 mD to 1.02 mD) after 180 days of exposure. This permeability decrease was close to the experimental results (from 1.60 mD to 0.80 mD) reported by Soong et al. (2014).

3.3 Sensitivity analysis results

Figure 4 shows results of sensitivity analysis considering the influence of aqueous CO₂ concentration (Figure 4a), initial porosity (Figure 4b), feldspar content (Figure 4c), annite content (Figure 4d), K_{eq} (SiO₂ (am)) (Figure 4e), k (SiO₂ (am)) (Figure 4f), and exponent n for permeability calculation (Figure 4g). An increase in aqueous CO₂ concentration resulted in slight increase of permeability, because an increase in aqueous CO₂ concentration decreases pH, which favors mineral dissolution. When initial porosity was low (5%), the permeability was increased instead of decrease after exposure, because the porosity increase in the high-porosity zone was relatively high given low initial porosity and the permeability increase of the high-porosity zone overcomes the permeability decrease of the low-porosity zone, which contributes to an overall

permeability increase. When initial porosity was very high, the permeability was less decreased compared with the base case after exposure. The permeability of the sample decreased from 1.6 mD to 1.26 mD after 180 days of exposure if the initial porosity of the sample was 30%, while the permeability of the sample decreased from 1.6 mD to 1.02 mD after 180 days of exposure if the initial porosity was 7.9%. Those results can be explained as: less initial pore space means that the pore space is more readily filled with precipitates, and the corresponding permeability drop will be more significant.

Initial feldspar content, $K_{eq}(\text{SiO}_2(\text{am}))$ and $k(\text{SiO}_2(\text{am}))$ had a big impact on the modeled permeability change of the sandstone, because these parameters are directly correlated with how much and how fast $\text{SiO}_2(\text{am})$ can precipitate. An increase of initial annite content resulted in an increase of permeability after exposure. The reason is: annite dissolves fast given a low pH and annite dissolution causes significant porosity and permeability increase of the high-porosity zone. Though a higher initial annite content provides more Fe^{2+} and enables more precipitation of siderite in the low-porosity zone, the permeability increase of the high-porosity zone still overcomes the permeability decrease of the low-porosity zone, which contributes to an overall permeability increase. The change of exponent (n) for permeability calculation had a moderate impact on permeability result after exposure.

3.4 Long-term permeability and porosity change

Figure 5a shows model-predicted permeability changes of the Mount Simon sandstone sample exposed to CO_2 -saturated brine for 5 days, 180 days and 30 years. After 30 years of exposure, the modeled permeability of the sample dropped to 0.003 mD, which is mainly attributed to the

occupation of pore space in the region about 0.2 mm from the sample surface (Figure 5b). The pore space occupation was primarily due to precipitation of SiO_2 (am) and kaolinite in the region. Compared with the scenario with 180 days of exposure, much more SiO_2 (am) and kaolinite is formed in the low-porosity zone after 30 years of exposure. The excessive precipitation of SiO_2 (am) and kaolinite causes significant porosity decrease of the low-porosity zone, which contributes to a significant permeability decrease of the entire sample after 30 years of exposure.

4. Discussion

The model predicts SiO_2 (am) and kaolinite formation as a result of interaction between sandstone and CO_2 -saturated brine after 180 days of exposure, and the formation of SiO_2 (am) and kaolinite is the primary cause of porosity and permeability drop of the sandstone. Formation of SiO_2 (am) and kaolinite in the pore space of feldspar-bearing sandstone under CO_2 sequestration conditions has been suggested by several modeling and experimental studies (Gaus et al., 2005; Lagneau et al., 2005; Fu et al., 2009; Shao et al., 2010; Carroll et al., 2012). Though the initial brine compositions, pressure and temperature applied in aforementioned references may differ from the conditions applied in this study, the results in aforementioned references demonstrate that precipitation of SiO_2 (am) and kaolinite can be observed in a broad range of CO_2 sequestration conditions, so SiO_2 (am) and kaolinite precipitation should be considered when our model is set up. The formation of SiO_2 (am) requires abundant SiO_2 (aq) and the formation of kaolinite requires abundant SiO_2 (aq) and Al (III) (aq) . SiO_2 (aq) mainly comes from dissolution of feldspar and quartz, and Al (III) (aq) mainly comes from dissolution of feldspar.

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378 The model also predicts formation of very small amount of muscovite/illite. Precipitation of
379 muscovite/illite is possible given large content of K-bearing feldspar in the sample and pore-
380 filling due to muscovite/illite precipitation under CO₂ sequestration conditions has been reported
381 before (Johnson et al., 2004; Fu et al., 2009). If a different geochemical model that predicts
382 significant precipitation of muscovite/illite is applied, the porosity and permeability of the
383 sample might be reduced more after exposure because muscovite/illite has a larger molar volume
384 (144.5 cm³/mol) than kaolinite (99.3 cm³/mol) and SiO₂ (am) (22.7 cm³/mol). Another
385 possibility is montmorillinite (Ca_{0.165}Mg_{0.33}Al_{1.67}Si₄O₁₀(OH)₂) precipitation. Pore-filling due to
386 montmorillinite precipitation under CO₂ sequestration conditions is suggested by Carroll et al.
387 (2012) and Beyer et al. (2012). If a different geochemical model that predicts significant
388 precipitation of montmorillinite is applied, the porosity and permeability of the sample might be
389 reduced more after exposure because montmorillinite has a larger molar volume (155.8 cm³/mol)
390 than kaolinite and SiO₂ (am).

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392 Though abundant CO₂ (aq) is present in the sandstone-CO₂-brine system, the model predicts no
393 formation of Ca-bearing carbonate mineral species (e.g., calcite and dolomite), which is
394 consistent with previous modeling studies and experimental observations (Johnson et al., 2004;
395 Carroll et al., 2012; Soong et al., 2014). That is to say, no or very small amount of Ca-bearing
396 carbonate species will be formed in the host rock (given several months of exposure period) if
397 CO₂ is injected into the Illinois Basin, from which the Mount Simon sandstone samples were
398 taken. Ca-bearing carbonate species may form at the surface of the sandstone in contact with the

bulk brine as a transient product, but the low pH at the surface (around 4.1) will finally dissolve any Ca-bearing carbonate species that are formed.

Other than SiO_2 (am) and kaolinite formation, two other factors that are not considered in the model (fine particle migration and dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) precipitation) may be considered as possible cause of the observed decrease of porosity and permeability of the sandstone sample after 180 days of exposure. The dissolution of minerals at the sandstone surface could result in breakdown of the structural integrity of the sandstone matrix and release of fine sandstone particles. The fine particles released may migrate in the direction of decreasing pressure and deposit in the region next to the high-porosity zone at the surface, thereby blocking those pore spaces and reducing the porosity in the region adjacent to the high-porosity zone. As for dawsonite precipitation, many modeling studies in the past have suggested that the precipitation of dawsonite is possible under CO_2 sequestration conditions (e.g., Xu et al., 2004; Johnson et al., 2004; Xu et al., 2005; Knauss et al., 2005; White et al., 2005; Audigane et al., 2007; Liu et al., 2011). The sandstone sample contains 13.8 vol% feldspar and the brine in contact with the sandstone sample contains 1.80 m Na^+ , which implies that Al and Na sources are abundant for dawsonite precipitation. Though dawsonite precipitation under CO_2 sequestration conditions is thermodynamically favorable, it has not been observed in experimental studies and the reliability of the equilibrium constant for dawsonite precipitation reaction used in past modeling studies has been challenged (Kaszuba et al., 2011). It is, therefore, believed to be unlikely that dawsonite

formation will proceed to an appreciable extent and, therefore, unlikely that this would be the cause of observed reductions in Mount Simon sandstone permeability (Soong et al., 2014).

The porosity of the Mount Simon sample used in this study is 7.9%. This porosity is quite low and is not representative of the porosity of typical CO₂ storage formations (14% to 35%, Rochelle et al., 2004; Johnson et al., 2004; Hovorka et al., 2006). However, given the highly variable porosity and permeability of the Mount Simon formation, there is a potential for CO₂ plume and CO₂-saturated brine to migrate from the storage region of Mount Simon to surrounding regions with low porosity, which is the scenario of this study. The results presented in this manuscript show that if the regions surrounding the storage region have a porosity of ~8%, there will be a significant reduction of permeability and that will be beneficial for CO₂ containment. The model predicts a significant porosity and permeability reduction of the sandstone after 30 years of exposure, which implies that the CO₂ injected into the Mount Simon formation can be securely retained. Specifically, after the period of active injection, CO₂-saturated brine would be relatively static and the formation of SiO₂ (am) and kaolinite could proceed to a significant extent. The formation of a SiO₂ (am) and kaolinite -rich layer with low porosity and permeability would act as a barrier to impede further lateral migration of both free-phase CO₂ plume and CO₂-saturated brine. As such, the formation of SiO₂ (am) and kaolinite in formations with the attributes described herein could have advantages for improved storage security. For the storage region of Mount Simon with a typical porosity of 30%, the effect of SiO₂ (am) and kaolinite precipitation has a smaller impact on the permeability (21% permeability reduction, see Figure 4b). Therefore, the chemical reactions between sandstone and CO₂-

saturated brine may have a small impact on the injectivity of the CO₂ storage intervals with high porosity and permeability.

5. Conclusions

Permeability decrease of Mount Simon sandstone samples after 180 days of exposure to CO₂-saturated brine is reproduced by a numerical model with the use of reactive transport code CrunchFlow. The measured permeability results show a permeability drop of Mount Simon sandstone samples from 1.60 mD to 0.80 mD after 180 days of exposure, while the model predicts a permeability decrease from 1.60 mD to 1.02 mD after 180 days of exposure. The model predicts that SiO₂ (am) and kaolinite are the primary minerals that cause permeability decrease, followed by the precipitation of muscovite/illite.

Based on sensitivity analysis results, initial porosity, initial feldspar content and precipitation rate constant of SiO₂ (am) are the three most important variables that affect permeability change. Permeability change is very sensitive to initial porosity because initial porosity is an important parameter in eqn. 4 to calculate permeability change. The most significant permeability decrease occurs when the initial porosity is between 6% and 10%. Permeability may increase instead of decrease when the initial porosity is small (less than 5%). Permeability change is sensitive to initial feldspar content because feldspar is the source of Si and Al for SiO₂ (am) and kaolinite precipitation. An increase of feldspar content results in decrease of permeability because more SiO₂ (aq) and Al (III) (aq) can be provided by feldspar to form SiO₂ (am) and kaolinite. Permeability change is also sensitive to precipitation rate constant of SiO₂ (am) because the rate

constant is used in eqn. 3 to calculate how fast SiO_2 (am) can precipitate. An increase of the precipitation rate constant of SiO_2 (am) from $10^{-7.09}$ mol/(m²s) to $10^{-6.09}$ mol/(m²s) results in the post-exposure permeability to drop from 1.02 mD to 0.46 mD. After 30 years of exposure, the permeability of sandstone is predicted to drop from 1.6 mD to 0.003 mD. In summary, if the sandstone surrounding the CO_2 storage formation has a porosity between 6% and 10% and is rich in feldspar, the CO_2 injected into the storage formation may be securely retained due to the permeability reduction of surrounding sandstone.

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References

- Adler, P.M., Jacquin, C.G., Thovert, J.F., 1992. The formation factor of reconstructed porous media. *Water Res. Res.*, 28 (6), 1571-1576.
- Andreani, M., Luquot, L., Gouze, P., Godard, M., Hoise, E., & Gibert, B., 2009. Experimental study of carbon sequestration reactions controlled by the percolation of CO_2 -rich brine through peridotites. *Environ. Sci. Technol.*, 43(4), 1226-1231.
- Archie, G.E., (1942. The electrical resistivity log as an aid in determining some reservoir characteristics. *Trans. AIME*, 146, 54-62.

488 Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T., 2007. Two dimensional
 489 reactive transport modeling of CO₂ injection in a saline aquifer at the Sleipner Site, North Sea.
 490 *Am. J. Sci.* 307, 974–1008.

491 Balashov, V. N., Guthrie, G. D., J. Hakala, A. J., Lopano, C. L., Rimstidt, D. J., and Brantley, S.
 492 L., 2013. Predictive modeling of CO₂ sequestration in deep saline sandstone reservoirs: Impacts
 493 of geochemical kinetics. *Appl. Geochem.* 30, 41–56.

494 Barlet-Gouédard, V., Rimmelé, G., Goffé, B. and Porcherie, O., 2007. Well Technologies for
 495 CO₂ Geological Storage: CO₂-Resistant Cement. *Oil Gas Sci. Technol.*, 62 (3), 325-334.

496 Baur, I., Keller, P., Mavrocordatos, D., Wehrli, B., and Johnson, C. A., 2004. Dissolution-
 497 precipitation behaviour of ettringite, monosulfate, and calcium silicate hydrate. *Cement Concrete*
 498 *Res.*, 34(2), 341-348.

499 Beyer, C., Li, D., De Lucia, M., Kühn, M., & Bauer, S., 2012. Modelling CO₂-induced fluid–
 500 rock interactions in the Altensalzwedel gas reservoir. Part II: coupled reactive transport
 501 simulation. *Environmental Earth Sciences*, 67(2), 573-588.

502 Bibi, I., Singh, B. and Silvester, E., 2011. Dissolution of illite in saline–acidic solutions at 25 °C.
 503 *Geochim. Cosmochim. Ac.*, 75(11), 3237-3249.

504 Brgm, 2011. THERMODDEM: A thermodynamic database for modeling the alteration of wastes
 505 minerals. Available at: <http://thermoddem.brgm.fr/index.asp?langue=GB>. Last accessed:
 506 02/20/2014.

507 Bruggeman, D.A.G., 1935. Berechnung verschiedener physikalischer Konstanten von
 508 heterogenen Substanzen. *Ann. Phys.*, 24, 636-664.

509 Brunet, J. P. L., Li, L., Karpyn, Z. T., Kutchko, B. G., Strazisar, B. and Bromhal, G., 2013.
 510 Dynamic evolution of cement composition and transport properties under conditions relevant to
 511 geological carbon sequestration. *Energ. Fuel.*, 27(8), 4208-4220.

512 Caseri, W. R., Shelden, R. A. and Suter, U. W., 1992. Preparation of muscovite with ultrahigh
 513 specific surface area by chemical cleavage. *Colloid Polym. Sci.*, 270(4), 392-398.

514 Casey, W.H., Westrich, H.R., Holdren, G.R., 1991. Dissolution rates of plagioclase at pH = 2
 515 and 3. *Am. Mineral*, 76, 1-2.

516 Carroll, S. A., & Walther, J. V., 1990. Kaolinite dissolution at 25, 60, and 80 °C. *Am. J. Sci*,
 517 290(7), 797-810.

518 Carroll, S. A., McNab, W. W., Dai, Z., and Torres, S. C., 2012. Reactivity of Mount Simon
 519 sandstone and the Eau Claire Shale under CO₂ storage conditions. *Environ. Sci. Technol.*, 47(1),
 520 252-261.

521 Craft, B. C., Hawkins, M. F., Terry, R. E., 1991. Applied Petroleum Reservoir Engineering.
522 Prentice Hall, Englewood Cliffs, NJ, p 431.

523 Crandell, L. E., Ellis, B. R. and Peters, C. A., 2009. Dissolution potential of SO₂ co-injected with
524 CO₂ in geologic sequestration. Environ. Sci. Technol., 44(1), 349-355.

525 Computer Support Group, Inc., 2014. Water Density Calculator. Available at:
526 <http://www.csgnetwork.com/h2odenscalc.html>. Last accessed: 05/23/2014.

527 Duan, Z. H. and Sun, R., 2003. An improved model calculating CO₂ solubility in pure water and
528 aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem. Geol., 193(3), 257-
529 271.

530 Fu, Q., Lu P., Konishi, H., Dilmore, R., Xu, H., Seyfried, W. Zhu, C., 2009. Coupled alkali-
531 feldspar dissolution and secondary mineral precipitation in batch systems: 1. New experiments at
532 200°C and 300 bars. Chem. Geol., 258, 125-135.

533 Garcia, S., Rosenbauer, R. J., Palandri, J., & Mercedes Maroto-Valer, M., 2011. Experimental
534 and simulation studies of iron oxides for geochemical fixation of CO₂–SO₂ gas mixtures. Energ.
535 Procedia, 4, 5108-5113.

536 Gasda, S. E., Nordbotten, J. M. and Celia, M. A., 2008. Determining effective wellbore
537 permeability from a field pressure test: a numerical analysis of detection limits. Environ. Geol.,
538 54, 1207–1215.

539 Gaus, I., Azaroual, M. and Czernichowski-Lauriol, I., 2005. Reactive transport modelling of the
540 impact of CO₂ injection on the clayey cap rock at Sleipner (North Sea). Chem. Geol., 217(3),
541 319-337.

542 Gherardi, F., Audigane, P. and Gaucher, E. C., 2012. Predicting long-term geochemical
543 alteration of wellbore cement in a generic geological CO₂ confinement site: Tackling a difficult
544 reactive transport modeling challenge. J. Hydrol., 420, 340-359.

545 Global CCS Institute, 2011. The Global Status of CCS: 2011. Global CCS Institute, Canberra,
546 Australia, ISBN 978-0-9871863-0-0.

547 Grathwohl, P., 1992. Diffusion controlled desorption of organic contaminants in various soils
548 and rocks. 7th International Symposium on Water Rock Interactions, 1992, Park City, Utah,
549 USA.

550 Gunter, W. D., Wiwehar, B. and Perkins, E. H., 1997. Aquifer disposal of CO₂-rich greenhouse
551 gases: extension of the time scale of experiment for CO₂-sequestering reactions by geochemical
552 modelling. Mineral. Petrol., 59(1-2), 121-140.

553 Holloway, S., 1997. An overview of the underground disposal of carbon dioxide. *Energ. Convers.*
554 *Manage.*, 38, 193-198.

555 Hovorka, S. D., Benson, S. M., Doughty, C., Freifeld, B. M., Sakurai, S., Daley, T. M., Kharaka,
556 Y. K., Holtz, M. H., Trautz, R. C., Nance, H. S., Myer, L. R. and Knauss, K. G., 2006.
557 Measuring permanence of CO₂ storage in saline formations: the Frio experiment. *Environmental*
558 *Geosciences*, 13(2), 105-121.

559 Jeong, H. S. and Pecha, D. L., 2011. *Pipelines 2011: A Sound Conduit for Sharing Solutions*.
560 ASCE Publications, Reston, VA.

561 Johnson, J. W., Nitao, J. J., and Knauss, K. G., 2004. Reactive transport modelling of CO₂
562 storage in saline aquifers to elucidate fundamental processes, trapping mechanisms, and
563 sequestration partitioning. Lawrence Livermore National Laboratory report, UCRL-JRNL-
564 205627.

565 Johnson, J.W., Nitao, J.J., Morris, J.P., 2005. Modeling the long-term isolation performance of
566 natural and engineered geologic CO₂ storage sites. *Greenh. Gas Con. Technol.*, 9, 1315-1321.

567 Johnson, J. W., Nitao, J. J., & Morris, J. P., 2005b. Reactive transport modeling of cap rock
568 integrity during natural and engineered CO₂ storage. *Carbon Dioxide Capture for Storage in*
569 *Deep Geologic Formations*, Volume 2, Elsevier Ltd., Oxford, UK.

570 Karamalidis, A. K., Torres, S. G., Hakala, J. A., Shao, H., Cantrell, K. J., & Carroll, S., 2012.
571 Trace metal source terms in carbon sequestration environments. *Environmental science &*
572 *technology*, 47(1), 322-329

573 Kaszuba, J. P., Janecky, D. R., & Snow, M. G., 2005. Experimental evaluation of mixed fluid
574 reactions between supercritical carbon dioxide and NaCl brine: Relevance to the integrity of a
575 geologic carbon repository. *Chem. Geol.*, 217(3), 277-293.

576 Kaszuba, J. P., Viswanathan, H. S., & Carey, J. W., 2011. Relative stability and significance of
577 dawsonite and aluminum minerals in geologic carbon sequestration. *Geophys. Res. Lett.*, 38(8),
578 L08404.

579 Kharaka, Y. K., Cole, D. R., Thordsen, J. J., Gans, K. D. and R. Burt Thomas, R. B., 2013.
580 Geochemical Monitoring for Potential Environmental Impacts of Geologic Sequestration of CO₂.
581 *Rev. Mineral. Geochem.*, 77(1), 399-430.

582 Knauss, K. G., and Wolery, T. J., 1989. Muscovite dissolution kinetics as a function of pH and
583 time at 70 °C. *Geochim. Cosmochim. Ac.*, 53(7), 1493-1501.

584 Knauss, K.G., Johnson, J.W., Steefel, C.I., 2005. Evaluation of the impact of CO₂,
585 cocontaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of
586 CO₂. *Chem. Geol.* 217, 339–350.

587 Kummerow, J. and Spangenberg, E., 2011. Experimental evaluation of the impact of the
588 interactions of CO₂ - SO₂, brine, and reservoir rock on petrophysical properties: A case study
589 from the Ketzin test site, Germany. *Geochem., Geophys., Geosy.*, 12(5).

590 Kumpel, H. (editor), 2003. Thermo-hydro-mechanical coupling in fractured rock. Birkhauser
591 Verlag, Basel, Switzerland.

592 Lagneau, V., Pipart, A., & Catalette, H., 2005. Reactive Transport modelling and Long Term
593 Behaviour of CO₂ Sequestration in Saline Aquifers. *Oil Gas Sci. Technol.*, 60(2), 231-247.

594 Lichtner, P.C., 1992. Time-space continuum description of fluid/rock interaction in permeable
595 media. *J. Geophys. Res.*, 3135-3155.

596 Liu, F., Lu, P., Zhu, C., Xiao, Y., 2011. Coupled reactive flow and transport modeling of CO₂
597 sequestration in the Mt. Simon sandstone formation, midwest USA. *Int. J. Greenh. Gas Con.* 5,
598 294–307.

599 Liu, F., Lu, P., Griffith, C., Hedges, S. W., Soong, Y., Hellevang, H. and Zhu, C., 2012. CO₂-
600 brine-caprock interaction: reactivity experiments on Eau Clair Shale and a review of relevant
601 literature. *Int. J. Greenh. Gas Con.*, 7, 153-167.

602 Lu, J., Milliken, K., Reed, R. M., & Hovorka, S., 2011. Diagenesis and sealing capacity of the
603 middle Tuscaloosa mudstone at the Cranfield carbon dioxide injection site, Mississippi, USA.
604 *Environmental Geosciences*, 18(1), 35-53.

605 Luquot, L. and Gouze, P., 2009. Experimental determination of porosity and permeability
606 changes induced by injection of CO₂ into carbonate rocks. *Chem. Geol.*, 265(1), 148-159.

607 Luquot, L., Andreani, M., Gouze, P., & Camps, P., 2012. CO₂ percolation experiment through
608 chlorite/zeolite-rich sandstone (Pretty Hill Formation–Otway Basin–Australia). *Chemical*
609 *geology*, 294, 75-88.

610 Marty, N. C. M., Tournassat, C., Burnol, A., Giffaut, E., and Gaucher, E. C., 2009. Influence of
611 reaction kinetics and mesh refinement on the numerical modelling of concrete/clay interactions. *J.*
612 *Hydrol.*, 364 (1–2), 58–72.

613 Morris, J. P., McNab, W. W., Carroll, S. K., Hao, Y., Foxall, W., & Wagoner, J. L., 2009.
614 Injection and reservoir hazard management: the role of injection-induced mechanical
615 deformation and geochemical alteration at In Salah CO₂ storage project: status report quarter end,
616 June 2009. LLNL Technical Report, doi: 10.2172/964517.

617

618 Oelkers, E. H., Schott, J., Gauthier, J. M. and Herrero-Roncal, T., 2008. An experimental study
619 of the dissolution mechanism and rates of muscovite. *Geochim. Cosmochim. Ac.*, 72(20), 4948-
620 4961.

621 Palandri, J. and Kharaka, Y. K., 2004. Compilation of rate parameters of water-mineral
622 interaction kinetics for application to geochemical modeling. In U.S. Geological Survey, Open
623 File Report 2004–1068; U.S. Geological Survey.

624 Palandri, J. L., & Kharaka, Y. K., 2005. Ferric iron-bearing sediments as a mineral trap for CO₂
625 sequestration: Iron reduction using sulfur-bearing waste gas. *Chem. Geol.*, 217(3), 351-364.

626 Parthasarathy, H., Tasneem, K., Dzombak, D. A., Karamalidis, A., 2011. Arsenic Dissolution
627 from Arsenopyrite Under Carbon Dioxide Geologic Sequestration Conditions. 2011 AGU Fall
628 Meeting, San Francisco, CA, USA.

629 Rochelle, C. A., Czernichowski-Lauriol, I., & Milodowski, A. E., 2004. The impact of chemical
630 reactions on CO₂ storage in geological formations: a brief review. Geological Society, London,
631 Special Publications, 233(1), 87-106.

632 Sel, O., Radha, A. V., Dideriksen, K., & Navrotsky, A., 2012. Amorphous iron (II) carbonate:
633 Crystallization energetics and comparison to other carbonate minerals related to CO₂
634 sequestration. *Geochim. Cosmochim. Ac.*, 87, 61-68.

635 Shao, H., Ray, J. R., & Jun, Y. S., 2010. Dissolution and precipitation of clay minerals under
636 geologic CO₂ sequestration conditions: CO₂– brine– phlogopite interactions. *Environ. Sci.*
637 *Technol.*, 44(15), 5999-6005.

638 Shen, D., Fu, G., Al-Saiari, H. A., Kan, A. T. and Tomson, M. B., 2009. Barite
639 dissolution/precipitation kinetics in porous media and in the presence and absence of a common
640 scale inhibitor. *SPE J.*, 14(03), 462-471.

641 Shimamura, K., 1992. Gas diffusion through compacted sands. *Soil Sci.*, 153 (4), 274-279.

642 Small, J. S., 1993. Experimental determination of the rates of precipitation of authigenic illite
643 and kaolinite in the presence of aqueous oxalate and comparison to the K/Ar ages of authigenic
644 illite in reservoir sandstones. *Clay. Clay Mineral.*, 41, 191-191.

645 Soong, Y., Howard, B. H., Hedges, S. W., Haljasmaa, I., Warzinski, R. P., Gino Irdi, G. and
646 McLendon, T. R., 2014. CO₂ sequestration in saline formation. *Aerosol Air Qual. Res.*, 14, 522-
647 532.

648 Steefel, C. I., 2009. CrunchFlow User’s Manual. Lawrence Berkeley National Laboratory,
649 Berkeley, CA.

650 Strang, G., 1968. On the construction and comparison of difference schemes, *SIAM J. Numer.*
651 *Anal.*, 506-517.

652 The North American Carbon Storage Atlas (NACSA), 2012. NACSA 2012 (1st Edition).
 653 Available at: [http://www.netl.doe.gov/File%20Library/Research/Carbon-](http://www.netl.doe.gov/File%20Library/Research/Carbon-Storage/NACSA2012.pdf)
 654 [Storage/NACSA2012.pdf](http://www.netl.doe.gov/File%20Library/Research/Carbon-Storage/NACSA2012.pdf).

655 Turcio, M., Reyes, J. M., Camacho, R., Lira-Galeana, C., Vargas, R. O., & Manero, O., 2013.
 656 Calculation of effective permeability for the BMP model in fractal porous media. *Journal of*
 657 *Petroleum Science and Engineering*, 103, 51-60.

658 Xu, T., Apps, J.A., Pruess, K., 2004. Numerical simulation of CO₂ disposal by mineral trapping
 659 in deep aquifers. *Appl. Geochem.* 19, 917–936.

660 Xu, T., Apps, J.A., Pruess, K., 2005. Mineral sequestration of carbon dioxide in a sandstone–
 661 shale system. *Chem. Geol.* 217, 295–318.

662 Xu, T., Zheng, L. and Tian, H., 2011. Reactive transport modeling for CO₂ geological
 663 sequestration. *J. Petr. Sci. Eng.*, 78(3), 765-777.

664 White, S.P., Allis, R.G., Moore, J., Chidsey, T., Morgan, C., Gwynn, W., Adams, M., 2005.
 665 Simulation of reactive transport of injected CO₂ on the Colorado Plateau, Utah, USA. *Chem.*
 666 *Geol.* 217, 387–405.

667 White, J. A., Borja, R. I., & Fredrich, J. T., 2006. Calculating the effective permeability of
 668 sandstone with multiscale lattice Boltzmann/finite element simulations. *Acta Geotechnica*, 1(4),
 669 195-209.

670 Wilson, A. M., Sanford, W., Whitaker, F., & Smart, P., 2001. Spatial patterns of diagenesis
 671 during geothermal circulation in carbonate platforms. *Am. J. Sci.*, 301(8), 727-752.

672 Wolery T.J., Jackson, K. J. , Bourcier, W. L., Bruton, C. J., Viani, B. E., Knauss, K. G., and
 673 Delany, J. M., 1990. Current Status of the EQ3/6 Software Package for Geochemical Modeling.
 674 ACS Symposium Series, 416, 104-116.

675 Yong, R. N., Mohaned, A.M.O. and Warkentin, B. P., 1992. Principles of Contaminant Transport
 676 in Soils. Elsevier, New York, NY.

677 Yu, Q. L. and Brouwers H. J. H., 2011. Microstructure and mechanical properties of beta-
 678 hemihydrate produced gypsum: An insight from its hydration process. *Constr. Build Mater.*, 25,
 679 3149-3157.

680 Zerai, B., Saylor, B. Z., & Matisoff, G., 2006. Computer simulation of CO₂ trapped through
 681 mineral precipitation in the Rose Run Sandstone, Ohio. *Appl. Geochem.*, 21(2), 223-240.

682 Zhang, L., Dzombak, D. A., Nakles, D. V., Brunet, J. P. L. and Li, L., 2013. Reactive Transport
 683 Modeling of Interactions between Acid Gas (CO₂ + H₂S) and Pozzolan-Amended Wellbore
 684 Cement under Geologic Carbon Sequestration Conditions. *Energ. Fuel.*, 27(11), 6921-6937.

685 Zysset, A., Stauffer, F. and Dracos, T., 1994. Modeling of chemically reactive groundwater
686 transport, Water Resources Res., 2217-2228.

Figure 1: Schematic of the modeling region.

Figure 2: a) Porosity change as a function of distance away from the sandstone surface; b) pH change as a function of distance away from the sandstone surface; c) total feldspar vol% change as a function of distance away from the sandstone surface; d) quartz vol% change as a function of distance away from the sandstone surface; e) annite vol% change as a function of distance away from the sandstone surface; f) muscovite vol% change as a function of distance away from the sandstone surface; g) siderite vol% change as a function of distance away from the sandstone surface; h) barite vol% change as a function of distance away from the sandstone surface; i) kaolinite vol% change as a function of distance away from the sandstone surface; j) SiO₂ (am) vol% change as a function of distance away from the sandstone surface; k) Schematic showing the locations of the high-porosity zone and the low-porosity zone.

Figure 3: a) Porosity distribution of the lowest-porosity location in Figure S-2 after 180 days of exposure. b) Permeability results of the sandstone sample exposed to CO₂-saturated brine for 180 days.

Figure 4: Sensitivity analysis results. a) Effect of aqueous CO_2 concentration (mol/kg) on permeability; b) effect of initial porosity change on permeability; c) effect of feldspar content change on permeability; d) effect of annite content change on permeability; e) effect of SiO_2 (am) equilibrium constant change on permeability; f) effect of SiO_2 (am) rate constant change on permeability; g) effect of exponent (n) change on permeability.

Figure 5: a) Model-predicted permeability change of the sandstone sample exposed to CO₂-saturated brine for 5 days, 180 days and 30 years; b) Model-predicted porosity change of the sandstone sample exposed to CO₂-saturated brine for 5 days, 180 days and 30 years.

Table 1: Brine composition reported by Soong et al. (2014) and brine composition used in the model, which takes account of mineral super-saturation at elevated temperature and injection of CO₂.

Brine composition in Soong et al. (2014) (measured at 25 °C; before injection of CO₂) Unit: mol/kg	Brine composition used in the model (calculated at 85 °C; after injection of CO₂) Unit: mol/kg
pH = 5.40	pH = 4.13
[H ⁺] = 3.59E-6	[H ⁺] = 7.41E-5
[Ca ²⁺] = 0.47	[Ca ²⁺] = 0.47
[Na ⁺] = 1.81	[Na ⁺] = 1.80
[Mg ²⁺] = 0.099	[Mg ²⁺] = 0.099
[K ⁺] = 0.036	[K ⁺] = 0.036
[Ba ²⁺] = 5.71E-5	[Ba ²⁺] = 9.64E-7
[SO ₄ ²⁻] = 4.84E-3	[SO ₄ ²⁻] = 4.78E-3
[H ₄ SiO ₄] = 1.61E-5	[H ₄ SiO ₄] = 6.24E-6
[Cl ⁻] = 2.97	[Cl ⁻] = 2.97
[Al ³⁺] = 1.00E-5	[Al ³⁺] = 1.15E-7
[Fe ²⁺] = 1.42E-3	[Fe ²⁺] = 1.42E-3
[CO ₂] _{tot} = N/A	[CO ₂] _{tot} = 0.689

Note: All values reported in Table 1 are in the unit of mol/kg. A brine density of 1.11×10^3 kg/m³ was used to convert mg/L values in Soong et al. (2014) into mol/kg. The brine density was calculated based on a brine density calculator (Computer Support Group, Inc., 2014).

Table 2: Mineral composition of unreacted Mount Simon sandstone and minerals produced as a result of the interaction between sandstone and CO₂-saturated brine. The composition of unreacted Mount Simon sandstone is assigned based on information in Carroll et al. (2012) and Soong et al. (2014).

Mineral name	Volume percentage (%, before reaction with brine and CO ₂)	Specific surface area (m ² /g)	Molar volume (cm ³ /mol)
Mineral composition of unreacted Mount Simon sandstone			
Na-rich feldspar (<i>NaAlSi₃O₈</i>)	12.9	0.39 ^a	100.4 ^b
Ca-rich feldspar (<i>CaAl₂Si₂O₈</i>)	0.26 ^c	0.39 ^a	100.4 ^b
Ba-rich feldspar (<i>BaAl₂Si₂O₈</i>)	3.97×10^{-3c}	0.39 ^a	100.4 ^b
Microcline (<i>KAlSi₃O₈</i>)	1.83	0.39 ^a	100.4 ^b
Quartz (SiO ₂)	77.0	0.10 ^d	22.7 ^d
Annite (<i>KFe₃AlSi₃O₁₀(OH)₂</i>)	0.11	7.43 ^e	154.3 ^f
Porosity	7.9	--	--
Minerals produced as a result of sandstone—brine interaction			
SiO ₂ (am)	0	1.62 ^e	22.7 ^d
Kaolinite (<i>Al₂Si₂O₅(OH)₄</i>)	0	15.0 ^h	99.3 ^f
Muscovite/Illite (<i>K_{0.85}Al_{2.85}Si_{3.15}O₁₀(OH)₂</i>)	0	3.40 ^g	144.5 ^d
Calcite (<i>CaCO₃</i>)	0	1.00 ^d	36.9 ^f
Gypsum (<i>CaSO₄ · 2H₂O</i>)	0	7.50 ⁱ	74.7 ^f
Barite (<i>BaSO₄</i>)	0	1.85 ^j	52.1 ^f
Siderite (<i>FeCO₃</i>)	0	9.8×10^{-4k}	29.4 ^f
Dolomite (<i>CaMg(CO₃)₂</i>)	0	0.10 ^l	64.3 ^f

Note:

a: The specific surface area of feldspar is the average of specific surface areas of 9 feldspar powder samples from Casey et al., (1991).

b: Molar volume assumed to be that of albite (Brgm, 2011).

c: Determined from elemental analysis data of the sandstone sample (Soong et al., 2014).

d: Information is from Marty et al. (2009).

e: Information is from Carroll et al. (2012).

f: Information is from Brgm (2011).

g: Information is from Caseri et al. (1992).

h: The specific surface area of kaolinite is between 10 and 20 m²/g (Yong et al., 1992). In this study, a value of 15 m²/g is used.

i: Information is from Yu and Brouwers (2011).

j: Information is from Shen et al. (2009).

k: Information is from Xu et al. (2005).

l: Information is from Wilson et al. (2001).

Table 3: Summary of important model parameters (equilibrium constants and rate coefficients).

$\prod_{i=1}^N a_i^{p_i}$ describes the effects of various ions in solution on the dissolution/precipitation rate.

Reaction	Equilibrium Constant at 85°C (K_{eq})	Rate Coefficient at 85°C, k , (mol/(m ² s) ^a	Value of $\prod_{i=1}^N a_i^{p_i}$
quartz dissolution/precipitation (85 °C) $SiO_2 + 2H_2O \leftrightarrow H_4SiO_4(aq)$	$10^{-1.81\ b}$	$10^{-11.38}$	1.0
SiO ₂ (am) dissolution/precipitation (85 °C) $SiO_2(am) + 2H_2O \leftrightarrow H_4SiO_4(aq)$	$10^{-2.84\ c}$	$10^{-7.09}$	1.0
Na-rich feldspar dissolution/precipitation (85 °C) $NaAlSi_3O_8 + 4H^+ + 4H_2O \leftrightarrow Na^+ + Al^{3+} + 3H_4SiO_4(aq)$	$10^{-0.64\ b}$	For pH-independent dissolution/precipitation, $k_1 = 10^{-11.29}$; For pH-dependent dissolution, $k_2 = 10^{-8.54}$.	For pH-independent dissolution/precipitation, $\prod_{i=1}^N a_i^{p_i} = 1.0$; For pH-dependent dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.5}$
Ca-rich feldspar dissolution/precipitation (85 °C) $CaAl_2Si_2O_8 + 8H^+ \leftrightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4(aq)$	$10^{16.53\ b}$	For pH-independent dissolution/precipitation, $k_1 = 10^{-11.29}$; For pH-dependent dissolution, $k_2 = 10^{-8.54}$.	For pH-independent dissolution/precipitation, $\prod_{i=1}^N a_i^{p_i} = 1.0$; For pH-dependent dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.5}$
Ba-bearing feldspar dissolution/precipitation (85 °C) $BaAl_2Si_2O_8 + 8H^+ \leftrightarrow Ba^{2+} + 2Al^{3+} + 2H_4SiO_4(aq)$	$10^{16.53\ d}$	For pH-independent dissolution/precipitation, $k_1 = 10^{-11.29}$; For pH-dependent dissolution, $k_2 = 10^{-8.54}$.	For pH-independent dissolution/precipitation, $\prod_{i=1}^N a_i^{p_i} = 1.0$; For pH-dependent dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.5}$
microcline dissolution/precipitation (85 °C) $KAlSi_3O_8 + 4H^+ + 4H_2O \leftrightarrow K^+ + Al^{3+} + 3H_4SiO_4(aq)$	$10^{-1.58\ b}$	For pH-independent dissolution/precipitation, $k_1 = 10^{-11.29}$; For pH-dependent dissolution, $k_2 = 10^{-8.54}$.	For pH-independent dissolution/precipitation, $\prod_{i=1}^N a_i^{p_i} = 1.0$; For pH-dependent dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.5}$

annite dissolution/precipitation (85 °C) $KFe_3AlSi_3O_{10}(OH)_2 + 10H^+ \leftrightarrow Al^{3+} + 3Fe^{2+} + K^+ + 3H_4SiO_4(aq)$	$10^{20.83\text{ e}}$	For pH-independent dissolution/precipitation, $k_1 = 10^{-11.49}$; For pH-dependent dissolution, $k_2 = 10^{-8.49}$	For reaction (1), $\prod_{i=1}^N a_i^{p_i} = 1.0$; For reaction (2), $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.53}$
kaolinite dissolution/precipitation (85 °C) $Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + H_2O + 2H_4SiO_4(aq)$	$10^{1.56\text{ b}}$	For dissolution, $k = 10^{-10.10}$; for precipitation, $k = 10^{-12.15}$	For dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]^{0.4}$; for precipitation, $\prod_{i=1}^N a_i^{p_i} = [Al^{3+}]$
barite dissolution/precipitation (85 °C) $BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$	$10^{-9.61\text{ b}}$	$10^{-2.97}$	$[Ba^{2+}][SO_4^{2-}]$
gypsum dissolution/precipitation (85 °C) $CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	$10^{-4.885\text{ b}}$	$10^{-4.16}$	1.0
siderite dissolution/precipitation (85 °C) $FeCO_3 + H^+ \leftrightarrow Fe^{2+} + HCO_3^-$	$10^{-1.20\text{ b}}$	$10^{-7.7}$	$[HCO_3^-]$
muscovite/illite dissolution/precipitation (85 °C) $KAl_3Si_3O_{10}(OH)_2 + 10H^+ \leftrightarrow 3Al^{3+} + K^+ + 3H_4SiO_4(aq)$	$10^{5.96\text{ b}}$	$10^{-10.33}$	1.0
dolomite dissolution/precipitation (85 °C) $CaMg(CO_3)_2 + 2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$	$10^{1.425\text{ b}}$	$10^{-14.43}$	1.0
calcite dissolution/precipitation (85 °C) $CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$	$10^{0.68\text{ b}}$	For dissolution, $k = 10^{-2.01}$; for precipitation, $k = 10^{-7.31}$	For dissolution, $\prod_{i=1}^N a_i^{p_i} = [H^+]$; for precipitation, $\prod_{i=1}^N a_i^{p_i} = [Ca^{2+}][HCO_3^-]$

Notes:

a: Details about the calculation of reaction rate constants can be found in Supporting Information.

b: Information is from Brgm (2011).

c: Reduced from the value of $10^{-1.56}$ in Carroll et al. (2012) to fit solution chemistry data.

d: K_{eq} for Ba-bearing feldspar dissolution reaction is assumed to be the same as that for Ca-rich feldspar dissolution reaction.

e: Here annite is used as a proxy of Fe-rich clay in the sandstone. The K_{eq} value is derived from Carroll et al. (2012).

Table 4: Justification to choose each parameter for sensitivity analysis and the values tested for each parameter

Parameter	Reason to test this parameter	Values tested
Initial concentration of dissolved CO ₂	Aqueous CO ₂ concentration determines pH, which determines how fast the feldspar can dissolve to provide H ₄ SiO ₄ (aq)	0.458, 0.689, 1.03, 1.378 mol/kg
Initial porosity	Important parameter in eqn. 4, which calculates permeability change	5, 6, 7.9, 10, 15, 30%
Initial feldspar content	Important parameter to determine how much feldspar can dissolve to provide H ₄ SiO ₄ (aq)	5, 15, 17, 20%
Initial annite content	The annite content determines how much aqueous iron can be provided to form siderite	0, 0.11, 1, 3, 5%
K _{eq} (SiO ₂ (am))	K _{eq} (SiO ₂ (am)) determines how fast SiO ₂ (am) can precipitate	10 ^{-2.78} , 10 ^{-2.84} , 10 ^{-2.86} , 10 ^{-2.90}
k(SiO ₂ (am))	k(SiO ₂ (am)) determines how fast SiO ₂ (am) can precipitate	10 ^{-6.09} , 10 ^{-6.59} , 10 ^{-7.09} , 10 ^{-7.59} , 10 ^{-8.09} , mol/(m ² s)
Exponent <i>n</i>	Important parameter in eqn. 4, which calculates permeability change	3, 6, 8, 11, 13, 15

Table 5: Comparison between model-predicted major element concentration and laboratory-measured major element concentration in brine after 180 days of exposure.

Element	Measured concentration (mg/kg water)	Model- predicted concentration (mg/kg water)
Ca	19725	18806
Na	35612	34143
Mg	2514	2376
K	1463	1458
Fe	92.7	128
Si	10.45	13.59