Reactive Transport Modeling for CO_2 Geological Sequestration

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Abstract. One way to reduce carbon dioxide (CO_2) releases to the atmosphere, is to capture it from power plants and then inject it into deep geological formations. Understanding water-gas-mineral reactions is the core of assessing the long term storage and risks in geological sequestration. Because of various limitations of laboratory and field tests, reactive transport modeling has been one important supplementary or independent tool to study the water-gas-mineral reactions at different components of geological sequestration. In this paper, we reviewed the applications of reactive transport modeling to three aspects of CO_2 geological sequestration: the behavior of CO_2 in storage formation, the storage security issues related to caprock integrity or wellbore cement degradation, and the change of the shallow groundwater in response to the potential leakage of CO_2. Key finding are summarized and further research needs are identified. The lack of the detailed mineralogical composition information at the storage formation, caprock and overlying aquifers is currently the first obstacle for quantitative prediction of geochemical evolution. The thermodynamic properties of relevant minerals under high temperature and pressure have to be refined. Reliable reaction rates of minerals dissolution/precipitation at field are still the bottle neck of the calculating the long term mineral trapping of CO_2. Issues related to relatively fast reactions such sorption and ion exchange need special attention when the impact of CO_2 leakage on shallow groundwater was evaluated. The role of organic compounds in water-gas-mineral reactions needs further study.

Key words: Reactive transport, CO_2 geological sequestration, Numerical modeling, Storage capacity, Caprock integrity, Groundwater quality

1. Introduction

A reduction in the release rate of carbon dioxide (CO_2) to the atmosphere is considered as an essential first step in the control of global warming. One way of achieving this is to inject CO_2 into deep geologic formations. Candidate formations include deep aquifers in sedimentary formations, caverns in salt/crystalline rock, structural traps in depleted oil and gas fields, and deep unmineable coal seams (Bachu et al., 1994). Injecting CO_2 into saline formations in sedimentary basins is one of the most promising methods of geological storage of CO_2 for the long-term sequestration of the gas. This is because saline formations are ubiquitous to sedimentary basins (Gunter et al., 2000), they have enough capacity to store large amounts of CO_2 from anthropogenic emissions, and there are shorter distances between most large CO_2 point sources and saline formations, which can minimize CO_2 transportation costs (Zerai et al., 2006).

Numerical modeling of reactive transport is necessary to evaluate the behavior and performance of the CO_2 injection, because many processes such as the slow aluminosilicate mineral alteration are not amenable to experimental study. Reactive transport modeling can be used to answer many questions and issues related to CO_2 geological sequestration.

First, reactive transport modeling is an important tool to study the fate and transport of injected CO_2, the amount of CO_2 dissolved in groundwater and trapped by carbonate minerals, and the variations of these trapping mechanisms over time. For this purpose, many reactive transport models have been reported such as for the Sleipner Site by Audigane et al. (2007), the Alberta Basin in Canada by Perkins et al. (2002), the Gulf Coast sandstone formation by Knauss et al., (2005) and Xu et al. (2004, 2005, 2006, and 2007), and the Ohio Basin by Zerai (2006).

Reactive transport modeling is also an important tool to study storage security issues related to, for example, caprock integrity or wellbore cement degradation. Long-term caprock integrity represents the single most important constraint on the long-term isolation performance of natural and engineered CO_2 storage sites. CO_2 influx that forms natural accumulations and CO_2 injection could lead to geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes (Johnson et al., 2005).

Although the risks of CO_2 geological sequestration to human health and the environment would be minimal with proper site selection and management of CO_2 storage projects, a risk remains that CO_2 could leak from a deep storage formation into overlying shallow potable groundwater aquifers. As a result, the CO_2 might spread out as gas phase as well as dissolved into the groundwater, which will subsequently cause an increase in the concentration of carbonic acid and decrease in pH. The pH decrease could mobilize trace elements through mineral dissolution, desorption reactions and/or exchange reactions (e.g. Aiuppa et al., 2005, Zheng et al. 2009, Apps et al. 2010). In addition, increases in dissolved CO_2 concentration could result in desorption of some elements such as arsenic by competitive sorption of carbonate ions (Appelo et al. 2002). The co-injected acid gases such as H_2S or SO_2, once leaking together with CO_2, are also likely to exacerbate the impacts on groundwater quality by the formation of strong metal-sulfide complexes (Zheng et al., 2010), reductive dissolution of metal-sorbing Fe(III) hydroxides, and/or strong effects of pH decrease from sulfide oxidation (Palandri and Kharaka, 2005; Xu et al. 2007). Reactive transport models, in the one hand, have been used a supplementary tools to interpret the field studies that were trying to address these issues (Ambats et at., 2009); on the other hand, provide generic or predictive study of the consequence of the CO_2 intrusion into the potable groundwater (Wang and Jaffe, 2004; Carroll et al., 2009; Apps et al., 2010; Zheng et a., 2009).

In this paper, we will present three modeling examples to illustrate the need of reactive transport modeling to (1) fate and transport of injected CO_2, (2) storage

security, (3) changes in groundwater quality in response to the potential CO_2 leakage.

The reactive transport simulator TOUGHREACT Version 2.0 was employed for the three examples. Description of the simulator is presented in Xu et al. (2011). Compared to the previous version of the simulator (Xu et al., 2006), major improvements related to CO_2 sequestration are as follows, (1) on reactive surface area algorithm for mineral-water reactions and fugacity coefficient corrections for gas-water reactions, (2) on mineral solid solution model that is an ideal model and only available for minerals reacting under kinetic constraints, and (3) in coupling and mass balances between the chemistry and physics parts, including changes in rock and fluid properties due to reactions, and accounting for CO_2 fixed as carbonates in the flow simulation. Equilibrium constants used for aqueous-aqueous and aqueous-mineral reactions in three examples are taken from Wolery (1992). A new fluid property module, ECO2N, based on work of Spycher and Pruess (2005) was used. This module provides an accurate description of the thermophysical properties of mixtures of water and CO_2 under conditions typically encountered in saline aquifers of interest for CO_2 sequestration ($31°C \leq T \leq 110°C$; $73.8 \text{ bars} < P \leq 600 \text{ bars}$).

2. Long-term fate of injected CO_2

The response of deep formations to CO_2 injection will depend on many factors, including formation permeability and porosity, the presence of heterogeneities such as faults and layers of high or low permeability, the physical and chemical characteristics of the brines, and the nature of the mineral phases that are present. A great deal of specific and detailed information will be required to assess the feasibility of storing CO_2 in a brine formation at any particular site, and to develop engineering designs for CO_2 storage systems.

Knauss et al. (2005) presented the results of reactive transport simulations to investigate the impact of mixtures of dissolved CO_2, H_2S, or SO_2 on a Texas Gulf coast sandstone formation. Audigane et al. (2007) presented a 2-D reactive transport

model of long-term geological storage of carbon dioxide, using a data set from the Utsira formation in Sleipner (North Sea). Zhang et al. (2009) performed reactive transport modeling to investigate long-term variations of CO_2 trapped in different mechanisms in deep saline formations using a sandstone case of the Songliao Basin of China. Liu et al. (2011) performed reactive transport simulations for large scale CO_2 injection (a million tons per year for 100 years) into Mt.Simon sandstone, a major candidate saline reservoir in the Midwest of USA. The long-term fate of CO_2 was simulated by extending the modeling period to 10,000 years. The results indicate that most of the injected CO_2 remains within a radius of 3300 m lateral distribution. Four major trapping mechanisms (hydrodynamic, solubility, residual, and mineral trapping) and their spatial and temporal variations are evaluated.

Here, a generic two-dimensional (2-D) radial model applicable to conditions encountered near the Texas gulf coast is taken to illustrate the temporal evolution and spatial distribution of the injected CO_2 and the subsequent physical and chemical changes (Figure 1). CO_2 injected into deep saline formations tends to migrate upward towards the cap-rock because the density of the supercritical CO_2 phase is lower than that of aqueous phase. In the upper portions of the reservoir, CO_2 dissolution into brine decreases pH and induces mineral dissolution and complexing with dissolved ions such as Na^+, Ca^{2+}, Mg^{2+}, and Fe^{2+} to form $NaHCO_3$, $CaHCO_3^+$, $MgHCO_3^+$, and $FeHCO_3^+$. The details on these reactions can be found in Rosenbauer et al. (2005) and Zhang et al. (2009). Over time these dissolution and complexing processes will increase CO_2 solubility, enhance solubility trapping, and will increase the density of the aqueous phase (Ennis-King and Paterson, 2007; Lindeberg and Wessel-Berg, 1997).

For numerical simulation, in the vertical direction a total of 20 model layers were used with a constant spacing of 2 m. In the horizontal direction, a radial distance of 100 km was modeled with a radial spacing that increases gradually away from the injection well. A total of 56 radial grid elements were used. The volume of the outer grid element is specified a large value of 10^{30} m^3, representing an infinite lateral boundary for constant pressure, temperature and concentrations. Injection of CO_2 was

applied at the bottom portion over 8 m thickness with a constant rate of 20 kg/s (corresponding to 0.64 Mt/year) for a period of 10 years. The 2-D radial model of fluid flow and reactive transport was simulated for a period for 1,000 years, which is a relevant time scale for CO_2 geological sequestration. We considered a system with initially homogeneous porosity and permeability. Changes in porosity and permeability due to mineral alteration could seed fluid dynamics instability and promote convective mixing. Hydrological and geochemical conditions and parameters were taken from Xu et al. (2006). The vertical permeability was decreased by one order of magnitude from the horizontal one (1×10^{-13} m^2). Mineral dissolution and precipitation were considered under kinetic conditions. Mineral composition and kinetic parameters can be found in Xu et al. (2006).

Simulation results indicate that the supercritical CO_2 fluid (called "gas" here for simplicity) injected at near the bottom of the storage formation migrates upward rapidly by buoyancy forces because the density of supercritical CO_2 phase is lower than that of aqueous phase (Figure 2). The combined effects of capillary pressure, salinity and in situ conditions on CO2-brine-rock interactions in saline aquifers have been discussed in detail by Alkan et al. (2010). A fraction of CO_2 gas, which is dependent on residual gas saturation (a value of 0.05 was used in the current simulation), is trapped in the porous rock as residual gas after injection. The residual gas trapping keeps CO_2 dissolving into brine and precipitating carbonate minerals, and gradually disappears at the bottom of the reservoir. With time most of the free CO_2 gas accumulates below the caprock, and then spreads laterally. To about 60 m radial distance along the formation bottom rock pores are completely filled by CO_2 gas at 10 years, or complete water drying-out zone. The vertical extent of the drying-out zone reaches the top of the reservoir but with a smaller radial distance of 25 m. After injection ends (at 10 years), groundwater re-invades previously dried-out zones and chemical reactions (dissolution and precipitation) between the dissolved CO_2 and minerals resume.

The simulated total dissolved CO_2 concentrations at different times are presented in Figures 3. With the migration of CO_2 gas, the concentration of dissolved

CO_2 rapidly increases to larger than 1 mol/kg H_2O in the two-phase region because of a high CO_2 partial pressure of about 200 bar there (the temperature is 75^oC, salinity is about 1.5). The injected CO_2 is dissolved in the surrounding formation water, forming H_2CO_3, HCO_3^-, and CO_3^{2-}, and decreasing pH, similar to Rosenbauer et al. (2005). Then, the increased acidity induces dissolution of many of the primary host rock minerals. The mineral dissolution increases concentrations of cations such as Na^+, Ca^{2+}, Mg^{2+}, and Fe^{2+}, which in turn forms aqueous complexes with the bicarbonate ion such as $NaHCO_3$, $CaHCO_3^+$, $MgHCO_3^+$, and $FeHCO_3^+$. Over time they tend to increase dissolved CO_2 (solubility) and enhance solubility trapping (Figure 3). Figure 3b shows "finger" flow patterns near the bottom of the CO_2 plume. These are because of advection in the aqueous phase that is triggered by an increase in density due to CO_2 dissolution. Note that modeling of CO_2 solubility and dissolution and precipitation of minerals are performed in a coupled manner.

The increased acidity (decreased pH) induces mineral dissolution and precipitation. Minerals such as oligoclase (Figure 4a) and chlorite (Figure 4b) dissolve in the two-phase region and near the front of the single aqueous-phase zone, supplying reactants for carbonate mineral precipitation.

Precipitation of carbonate minerals such as siderite (Figure 5a), ankerite (Figure 5b), and dawsonite (Figure 5c) occurs mainly at the front of the single aqueous-phase region because of higher pH there. At the same time, clay minerals such as smectite-Na precipitate (Figure 5d).

The mineral alteration pattern and comparison with field observations have been discussed in details in Xu et al. (2007). As discussed previously, dawsonite might be stable under high CO_2 partial pressures and moderately acid conditions. Moore et al. (2005) describe the formation of secondary dawsonite in siltstones of the Permian Supai Formation of the Springerville-St. John CO_2 field on the border between Arizona and New Mexico. They observed secondary dawsonite spatially associated with corroded oligoclase, which is consistent with our current and previous simulations.

Changes in porosity are calculated from variations in mineral volume fractions.

Porosity increases slightly in the two-phase region due to dominant mineral dissolution (Figure 6) caused by low pH. While porosity decreases at the front of the aqueous-phase because of higher pH and carbonate mineral precipitation. A simple cubic Kozeny-Carman grain model was used to calculate permeability. The pattern of permeability changes is similar to that of porosity.

Evolution of amounts of CO_2 trapped in the three phases over time is presented in Figure 7. In the CO_2 injection period (0-10 years), a large amount of injected CO_2 remains as a free supercritical phase (gas trapping). After the stop of injection, the mass of CO_2 dissolved in the formation water gradually increases because of (1) the upward and horizontal migration of CO_2 plume and the convective mixing between CO_2-saturated water and unsaturated water, and (2) density increases due to mineral dissolution and aqueous complexation. The amount of CO_2 mineral trapping starts at about 50 years when primary mineral dissolution has neutralized the pH, the mineral trapping increases gradually (almost linearly) with time. The inclusion of mineral dissolution and precipitation in the modeling are significant for (1) enhancing solubility trapping and (2) obtaining mineral trapping, which are important for long-term storage of CO_2 geological sequestration. After 1,000 years, 43% of the injected CO_2 is trapped in the gas phase, 28% in the aqueous, and 29% in the solid (mineral) phase. As discussed in Xu et al. (2004, 2005, and 2007), variations in the reaction rate and abundance of chlorite, and plagioclase composition affect significantly the estimates of mineral alteration and CO_2 storage in different trapping mechanisms.

Mineral alteration and CO_2 trapping capability depends on the primary mineral composition. Precipitation of siderite and ankerite requires Fe^{2+}, which can be supplied by the dissolution of iron-bearing minerals, such as chlorite, or by reduction of Fe^{3+} in small amounts of hematite. Variation in Ca content in plagioclase significantly affects carbonate mineral precipitation, and thus CO_2 mineral trapping. The time required for mineral alteration and CO_2 sequestration depends on the rates of mineral dissolution and precipitation.

3. Storage security

Key issues in a quantitative assessment of the sealing efficiency of caprock formations can be addressed by reactive transport modeling. The impacts of dissolution processes of caprock formations by acidic CO_2-rich fluids can be evaluated. Reactions induced by CO_2 in rocks filled with saline waters likely involve acid hydrolysis of rock-forming minerals. Dissolution reactions are likely when gas breakthrough is expected in carbonate-rich rocks, with both the type and timing of the mineralogical alteration in caprocks being highly variable and specific to geochemical, physical and hydrologic features of the investigated systems. Mineral alteration of caprock formations induced by CO_2 injection can change interfacial tension and wettability behavior (Hildebrand et al., 2004).

Johnson et al. (2005) used a reactive transport model to assess the evolution of cap-rock permeability due to CO_2 injection induced mineral alteration. Gherardi et al. (2007) presented numerical simulations of reactive transport which is induced in the caprock of an on-shore depleted gas reservoir by the geological sequestration of carbon dioxide.

In this paper, we will give an example similar to the case of Gherardi et al. (2007) to illustrate how reactive transport modeling can answer questions related to changes in sealing capacity of a caprock formation due to CO_2 injection. We used a shale layer of US Gulf Coast as a caprock formation overlaid a sandstone storage reservoir (Xu et al., 2005).

A simplified 1-D model is used with sandstone reservoir as the bottom boundary of the shale system. The 1-D model consists of 15 vertical elements of 1 m^2 cross-sectional area through the caprock. The volume of the reservoir block is 1×10^{10} m^3, while the caprock has been discretized using small grid spacing of the order of a few mm near the bottom, to better resolve chemical concentration gradients near the bottom boundary.

Hydrological parameter specification and mineral composition for sandstone

and shale layers were chosen to represent conditions encountered in Texas Gulf Coast sediments at a depth of order 2 km (Xu et al. 2005). A porosity of 0.3 was used for sandstone, and a porosity of 0.1 for shale.

The reservoir is initialized in two-phase conditions with initial CO_2 gas saturation S_g=0.5, whereas the caprock is assumed to be fully liquid-saturated (S_l=1.0). The duration of the simulation is 1000 years.

Results indicate that when fluid-rock interactions occur under fully liquid-saturated conditions in the caprock in a diffusion-controlled regime, pH will be buffered at high values, and precipitation of ankerite and smectite-Na is predicted (Figure 8). The precipitation drives dissolution of minerals such as oligoclase and chlorite (Figure 9). Overall the precipitation dominates dissolution, resulting in decreases in porosity (Figure 10) penetrating about 4 m into the caprock and further sealing of the storage reservoir.

Fluid-rock interactions in fractured caprock have been modeled through a simplified 2-D model similar to Gherardi et al. (2007), which consider idealized fractured rocks with single or multiple vertical fracture zones of variable aperture and spacing. The modeling results of the fractured caprock case with the same mineral composition indicate that when a free CO_2-dominated phase migrates into the shale caprock through pre-existing fractures, or through zones with high initial porosity acting as preferential flow paths for reservoir fluids, low pH values where supercritical CO_2 is able to flow, are predicted, accompanied by significant mineral dissolution and porosity enhancement (Figure 11). The self-limiting behavior of this case is in contrast to the self-enhancing (or self-sealing) alteration of the tight caprock case as mentioned above.

The example shows that variations with time in the sealing capacity of the caprock can be evaluated using reactive transport modeling. The occurrence of some CO_2 leakage from the reservoir may have a strong influence on the geochemical evolution of the caprock.

In the framework of activities related to wellbore integrity and risk assessment for the storage site, an important potential escape mechanism is the CO_2 leakage via

poorly plugged or old abandoned wells. The long-term stability of wellbore materials in a CO_2-rich environment is another key issue concerning wellbore integrity (Geloni et al., 2011; Metz et al., 2005; Viswanathan et al., 2008; Carey et al., 2010). The primary paths for CO_2 migrations along the well are the interfaces, either the casing-cement or the cement-caprock, rather than the flow through the CO_2 resistant matrix cement that can in fact, at least in the short term, provide an effective barrier. The topic can be studied by reactive transport modeling, in addition to laboratory experiments. Geloni et al. (2011) performed the numerical modeling to investigate the rock-cement alterations driven by the injection of CO_2. Their simulations were able to predict the main mineralogical alterations occurring at the cement-reservoir and cement-caprock interfaces as documented in the literature (as muscovite dissolution and zeolites and brucite precipitation, Gaucher and Blanc, 2006). The cement alterations due to CO_2 brine acidification are very localized at the rock domain interfaces.

4. Impact of potential CO_2 leakage on the groundwater quality

Reactive transport model have been used to evaluate the potential effect of CO_2 leakage on the groundwater. Wang and Jaffe (2004) were one of the pioneers of conducting reactive transport simulations to assess such issue. However, the authors intended their study only to illustrate the potential adverse effects of CO_2 intrusion on water quality. Their simulations did not necessarily represent realistic conditions as their model geochemical system was greatly simplified. They assumed that the aquifer was only composed of quartz, and/or calcite and unrealistic high content of galena. The decrease of pH induced significant dissolution of galena and subsequently very high lead concentration. Thus, while Wang and Jaffe (2004) highlighted a potential concern, it was not clear to how severe and widespread the problem would be in reality. Carrol et al. (2009) conducted reactive transport simulations to evaluate the impact of CO_2 intrusion into the High Plains Aquifer in the United States to evaluate the pH and alkalinity response of a large aquifer to CO_2 intrusion. Their study was useful to assess CO_2-induced pH variations over large scales and implications for monitoring CO_2 leakage, although other aspect of water quality such as the potential increase of the concentration of trace elements was not addressed therein.

Birkholzer et al. (2008) conducted a systematic evaluation of the possible water quality changes in response to CO_2 intrusion into potable water aquifers in the United States. A comprehensive thermodynamic analysis of a large number of groundwater compositions was conducted (Apps et al., 2010) followed by systematic reactive transport simulations of hypothetical leak scenarios (Zheng et al., 2009). These investigations showed that CO_2 leakage into a shallow aquifer could lead to mobilization of hazardous trace elements, in particular As and Pb. Recently Zheng et al. (2010) indicates that co-injected H_2S could exacerbate the adverse effect of CO_2 on groundwater quality. In this paper, we use some work from Birkholzer et al. (2008) to illustrate how reactive transport models were used to evaluate the impact of potential

CO_2 leakage on the groundwater quality and the challenges confronted when developing such models.

Because the work in Birkholzer et al. (2008) was a generic study rather than dedicated to a particular site, the hydrogeological setup, as illustrated in Figure 12, is rather simple, assuming a confined aquifer with a uniform vertical thickness of 10 m at a reference depth of 50 m. The simulation domain comprises an area of 500 m in length and 200 m in width. Water flows from left to right with a pore velocity of 10 m per year. CO_2 is assumed to migrate from a deeper geological storage site into the aquifer, representing, for example, a local leakage through a fault zone. It is assumed that CO_2 continuously leaks into the aquifer with a rate of 7.5×10^{-5} kg/s, which corresponds to 2.36 tonnes per year.

The chemical reactions considered in the model include aqueous complexation, minerals dissolution/precipitation and adsorption/desorption via surface complexation. It is assumed that arsenian pyrite is the mineral phase that controls the aqueous As by the following reaction (Zheng et al., 2009):

$$FeAs_{0.05}S_{1.95} + 1.025\ H_2O + 0.0375\ O_2(aq) = 1.0000\ Fe^{+2} + 0.1875\ H^+ + 0.2375\ SO_4^{-2} + 1.7125\ HS^- + 0.0500\ H_3AsO_3(aq) \quad (1)$$

The stoichiometry of the arsenian pyrite is based conservatively on the assumption that the initial concentration of As assumed to be present in crustal rocks is concentrated wholly in 1 wt.% pyrite in the aquifer host rock. It is also assumed that galena provides the solubility control of Pb under the anoxic conditions by the reaction:

$$PbS + 2H^+ = H_2S(aq) + Pb^{+2} \quad (2)$$

in conformity with the results obtained by Hsieh and Huang (1989). The adsorption of lead and arsenic on goethite, illite, kaolinite, and smectite are considered in the model. A complete list of relevant surface complexation is given in Zheng et al. (2009).

When a reactive transport model is employed to evaluate the impact of CO_2 on groundwater, the very first step is to setup the baseline geochemical condition of the

aquifer prior to the leakage of CO_2. This includes the mineralogical composition of aquifer, the aqueous composition of the groundwater and the distribution of the trace elements between different phases. Three types of aquifer have been considered in Birkholzer et al., (2008) and here we will focus on the one type, or the St Peter Sandstone in Illinoise Basin (Pitman et al., 1997). The mineralogical composition is listed in Table 1. The aqueous composition of the groundwater was obtained by an initial equilibrium simulation, which was conducted using the mineralogical composition to establish a quasi-steady-state chemical composition of the groundwater. The calculated water composition is listed in Table 2.

Because the dissolution of CO_2 into aqueous phase is much faster comparing to transport processes, the kinetics of dissolution of CO_2 into aqueous phase is assumed at local equilibrium. The CO_2 intruding into the aquifer therefore dissolves instantaneously into the groundwater. The plume of dissolved CO_2 migrates primarily along the groundwater flow direction, while lateral spreading of dissolved CO_2 is minor. The evolution of pH closely follows the evolution of dissolved CO_2. Figure 13 shows the simulated pH in profiles along the x-axis at y=0 m for different times. Note that the pH close to the intrusion location is significantly smaller at 100 years than at 50 years. This further pH drop is caused by the partial loss of pH buffer capability as the initially small volumes of calcite and dolomite minerals dissolve and eventually become depleted close to the intrusion location and the immediate downstream region.

Desorption/adsorption via surface complexation might be the most important process controlling the fate of hazardous trace elements mobilized by CO_2 leakage (Zheng et al., 2009). The complex interaction between desorption/adsorption, dissolution/precipitation of relevant minerals, and the dissociation/association of aqueous complexes control changes in aqueous Pb concentration in response to CO_2 intrusion. Figure 14 shows the resulting Pb concentrations at different times after CO_2 intrusion, exhibiting a complex transient behavior. Early on, the Pb concentrations increase strongly close to the intrusion location, but decrease at later stages. From the observed evolution of pH, which decreases further at later stages because buffering

minerals become depleted, one would have expected the opposite behavior because further drop of pH would result in further increase of lead concentration. Analysis of the adsorption characteristics for lead reveals that the trend of decreasing lead concentrations close to the intrusion location is caused by a corresponding depletion of Pb on adsorption sites. The early increase in aqueous Pb is mainly caused by desorption of initially sorbed Pb. However, the initial amount of sorbed Pb becomes fully depleted near the intrusion location after about 50 years, taking away a significant source of Pb in solid phase. Note that the predicted value is significantly higher (about one order of magnitude) than the initial concentration, but remains below the maximum contaminant level (MCL) defined by the U.S. Environmental Protection Agency (EPA), which is 7.24×10^{-8} mol/L (15 ppb) for Pb.

The model assumes that sorption via surface complexation is in equilibrium whereas mineral dissolution/precipitation is kinetically controlled, as is known that the time for an adsorption reactions to equilibrate is substantially shorter than that for mineral dissolution, in particular when low-solubility minerals such as sulfides are concerned (Selim and Amacher, 1996). The intrusion of CO_2 immediately disturbs both sorption and solubility equilibria, but whereas sorption re-equilibrate instantaneously, the dissolution/precipitation of a hazardous mineral host is much slower. The instantaneous release of Pb from sorption sites therefore increases the aqueous Pb concentration so significantly that the solution becomes transiently supersaturated with respect to galena. Therefore, galena precipitation occurs close to the intrusion location (even though the groundwater becomes more acidic, which could otherwise suggest undersaturation with respect to galena). However, as the sorbed lead deplete on the later stage (after 50 years), galena starts to dissolve.

A different behavior is seen in the As results. The As concentration in the groundwater increases strongly close to the intrusion locations between 50 years to 100 years (Figure 15), consistent with the further decrease of pH during this period. The obvious difference to the results observed for Pb is that there is enough As initially sorbed on mineral sites such that depletion of sorbed As is not an issue. The behavior of As also differs from that of lead in terms of minerals dissolution: arsenian

pyrite always dissolves because the release of arsenic from sorption site is not significant enough to change the saturation state of arsenic pyrite. As stated in Zheng et al. (2009), the relative effect of dissolution/precipitation versus desorption/adsorption was different for different species and determined by many factors, including adsorption parameters, reaction kinetics, aqueous complexation processes, and mineral solubility constants. Model results show that aqueous concentration of As is higher than MCL near the intrusion locations.

While such generic model studies illustrate the vulnerability of the given aquifer types in the case of CO_2 intrusion, the calculated values should be treated with great caution because the numerous uncertainties involved in the model. Although a comprehensive sensitivity study was conducted for different hydrological, geochemical, and mineralogical conditions (Birkholzer et al., 2008), it is understood that even the most comprehensive sensitivity study can neither encompass all possible conditions and scenarios, nor can it account for all relevant uncertainties. As stated in Apps et al. (2010), it was recommend that "the generic study should be followed up with site-specific model predictions, and that laboratory or field experiments should be performed to test uncertain model assumptions and parameters."

The huge uncertainties in reaction rate for mineral dissolution/precipitation are always a big obstacle for any meaningful prediction with reactive transport model, partially because the significant difference between the laboratory experiment-derived rates and field test-derived rate (e.g. Zhu, 2005). Moreover, another difficulty when applying reactive transport to evaluate the impact of CO_2 on groundwater is the lack of thermodynamic database for sorption reactions. Currently, the most comprehensive database for sorption reaction is the adsorption of various elements on iron hydroxide (Dzombak, and Morel, 1990). Clay minerals (Zheng et al., 2009), however, could also be the major adsorbent and even play more significant role than iron hydroxide. When trying to compile sorption data for clay, in addition to the very limit availability of sorption for some chemical species, special attention needs to be paid for unconsistence of published sorption data. Most lab experiments for determining the sorption data are conducted for the sorption of one particular species on one particular

mineral surface, these data are not necessarily consistent with each other when calculating the sorption of multi-species on multi-mineral surface. Probably that is why in some cases, the Generalized Composite approaches rather than the Component Additivity is preferred (Davis et al., 1998).

5. Discussions

Reactive transport modeling that provides valuable insights regarding the physical and chemical consequences of CO_2, are very useful tool for its geological sequestration, the need of the modeling is summarized in Table 3. The results are, however, constrained by parameter uncertainties to replicate all of the complex physical, hydrological and geochemical processes that are expected to occur. More experimental studies are needed to fill the gaps in our knowledge. Refinements on thermodynamic data especially for highly-concentrated solutions are needed. These can be addressed by lab experiments and using mineral alteration patterns observed in natural analogues of high-pressure CO_2 reservoirs. Further model and code development, such as introducing Pitzer ion-interaction model as used by Zhang et al. (2008), are necessary for evaluating CO_2 induced geochemical changes in high-salinity environments. Natural analogues provide useful information on geochemical processes occurring in natural environments that laboratory experiments may not be able to reproduce. Such information can assist in the calibration of geochemical models, allowing them to make accurate predictions at the timescales involved in nature (Haszeldine et al., 2005).

The time scale for significant convective mixing is likely to be slow (on the order of hundreds of years or more) as shown in the current study and in Ennis-King and Paterson (2007), and may be roughly comparable to time scales for significant geochemical interactions of CO_2.

Predicting the long-term changes in chemistry of fluid and mineral phases is especially challenging. These changes depend on many factors including initial abundance of primary minerals, and pressure and temperature conditions of storage

formation. The time frame for chemical and physical changes and CO_2 sequestration is a function of reaction kinetics of mineral dissolution and precipitation, which requires further study. Reactivity of supercritical CO_2 with rock and organic matters is not well understood. Experimental studies are required to quantitatively describe the reaction kinetics.

Evaluating the short-term chemical changes of shallow groundwater is facing slightly different challenges comparing with predicting the long-term chemical changes in the storage formation. It doesn't have to deal with high pressure and temperature conditions and therefore the thermodynamic database is more mature. Although reaction kinetics of mineral dissolution and precipitation (mainly the trace element bearing mineral rather than aluminosilicate) is important, some fast reactions such sorption and/or ion exchange might dampen the its importance. But special attention should be paid on the sorption (surface complexation) and ion exchange reactions: very detailed mineralogical characterization is needed; cation exchange capacity and sorption sites have to be measured; consistency of the surface complexation constants should be assured. In addition, CO_2 might bring a significant amount of organic compounds when CO_2 transport from storage formation to overlying shallow aquifer (Zheng et al., 2010). The organic compounds might greatly change the redox condition of the aquifer, enhance the solubility of trace element by aqueous complexation and alter the sorption behavior of trace elements, which still needs further study.

Issues on model validations are important if CO_2 injection technology is to be implemented safely, efficiently, and predictably. Validation of reactive transport models could be different from conventional model validation methods for groundwater flow and solute transport. For the short-term behaviors, the models can be validated using experimental data and field demonstration. For the long-term mineral alteration and CO_2 sequestration, the natural analogue using high-pressure CO_2 reservoirs could be a best way to validate the model.

6. Conclusions

Reactive transport modeling is an important tool to study the fate and transport of injected CO_2, the amount of CO_2 dissolved in groundwater and trapped by carbonate minerals, and the variations of these trapping mechanisms over time. The modeling is also an important tool to study storage security issues such as caprock integrity and wellbore cement degradation. The potential leakage from CO_2 storage formations into potable aquifers and its impact on the groundwater quality is another issue that can be addressed by reactive transport modeling.

In this paper, we reviewed the applications of reactive transport modeling to three aspects of CO_2 geological sequestration. Key finding are summarized and further research needs are identified. The lack of the detailed mineralogical composition information at the storage formation, caprock and overlying aquifers is currently the first obstacle for quantitative prediction of geochemical evolution. The thermodynamic properties of relevant minerals under high temperature and pressure have to be refined. Reliable reaction rates of minerals dissolution/precipitation at field are still the bottle neck of the calculating the long-term minerals trapping of CO_2. Issues related to relatively fast reactions such as sorption and ion exchange need special attention when the impact of CO_2 leakage on shallow groundwater was evaluated. The role of organic compounds in water-gas-mineral reactions needs further study.

The range of problems concerning reactive transport modeling is very broad. The simulation results presented here are specific to the conditions and parameters considered. Care should be taken when extrapolating the results and conclusions for other sites. However, reactive transport modeling is an excellent resource for evaluating storage capacity, security, and environmental impact for CO_2 geological sequestration. A critical evaluation of modeling results can provide useful insight into sequestration mechanisms and controlling hydrogeological and geochemical conditions and parameters.

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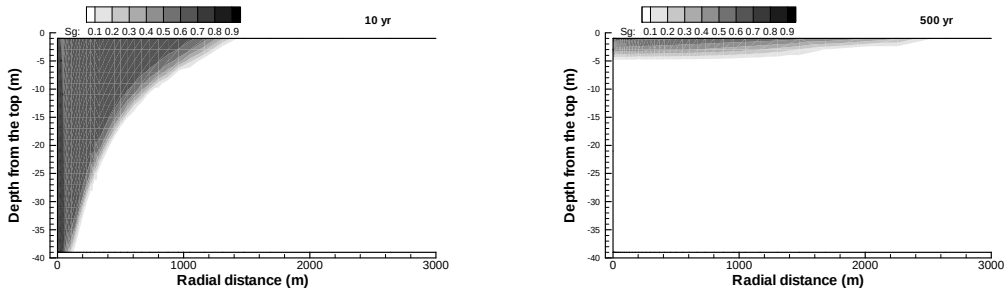
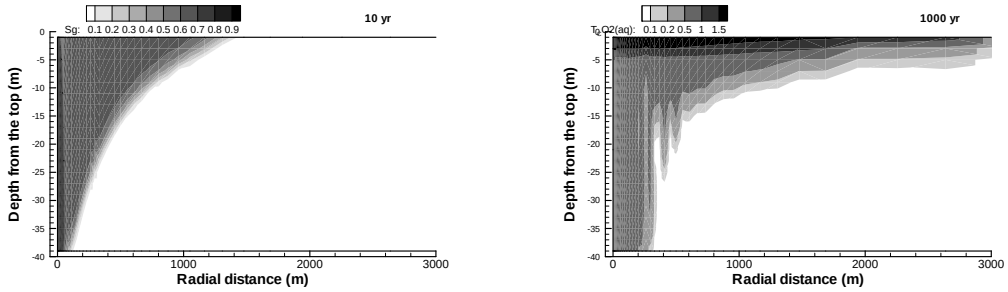


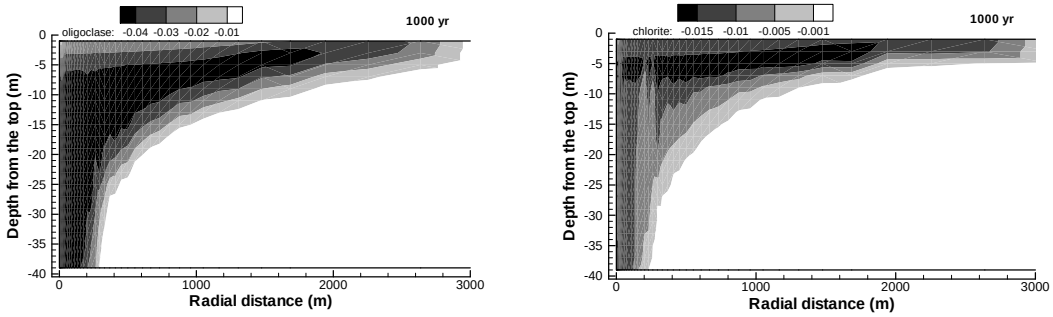
(a) 10 years (b) 500 years

Figure 2. Distribution of supercritical CO_2 gas phase saturation (Sg) at different times for the 2-D radial model.



(a) 10 years (b) 1,000 years

Figure 3. Distribution of total dissolved CO_2 (mol/kg H_2O) at 10 and 1000 yr.



(a) Oligoclase (b) Chlorite

Figure 4. Changes of volume fraction of oligoclase and chlorite (negative values indicate dissolution, positive precipitation) after 1,000 years.

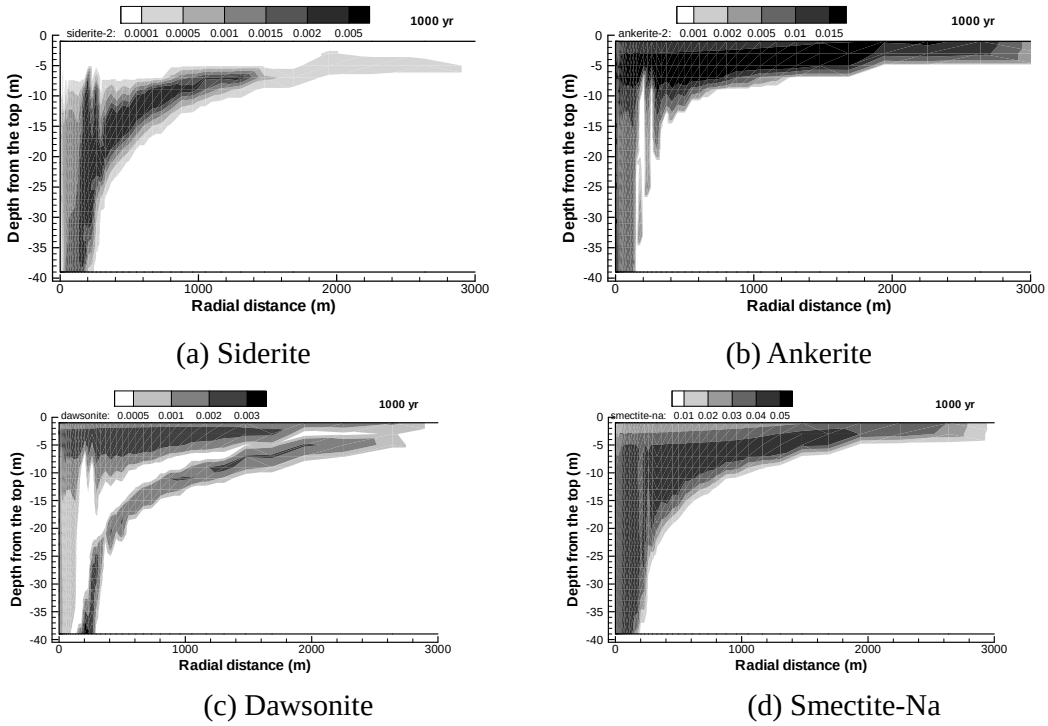
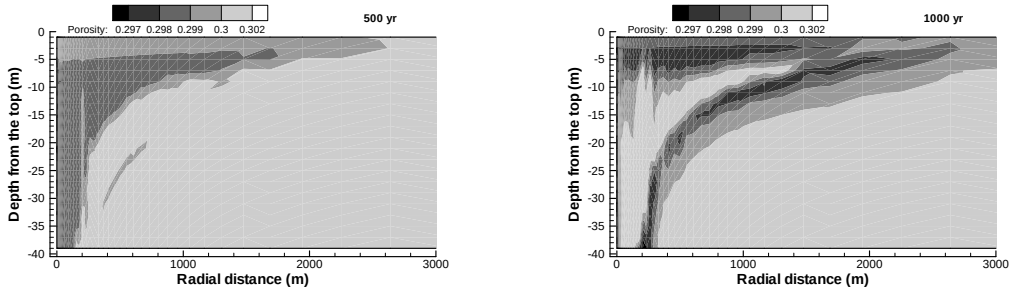


Figure 5. Changes of volume fraction of siderite, ankerite, dawsonite, and smectite-Na after 1,000 years.



(a) 500 yr (b) 1000 yr

Figure 6. Distribution of porosity after 500 and 1,000 years.

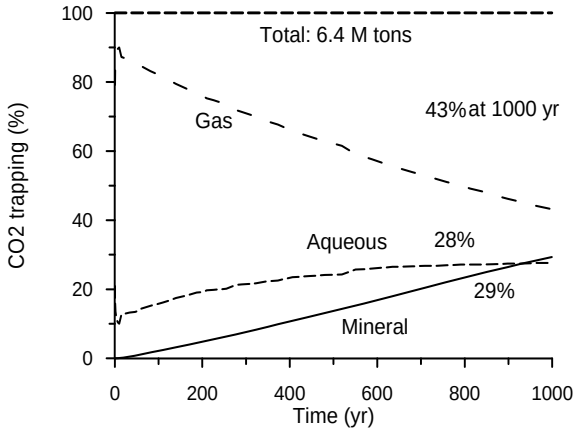
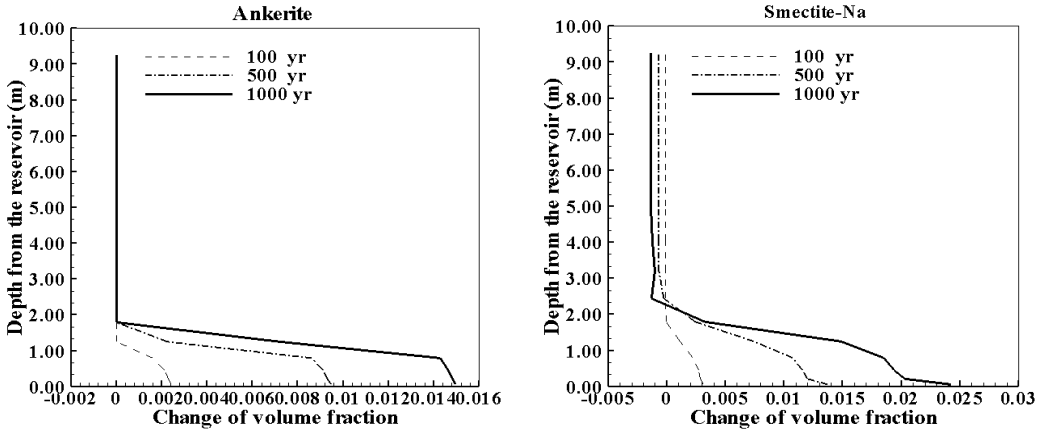
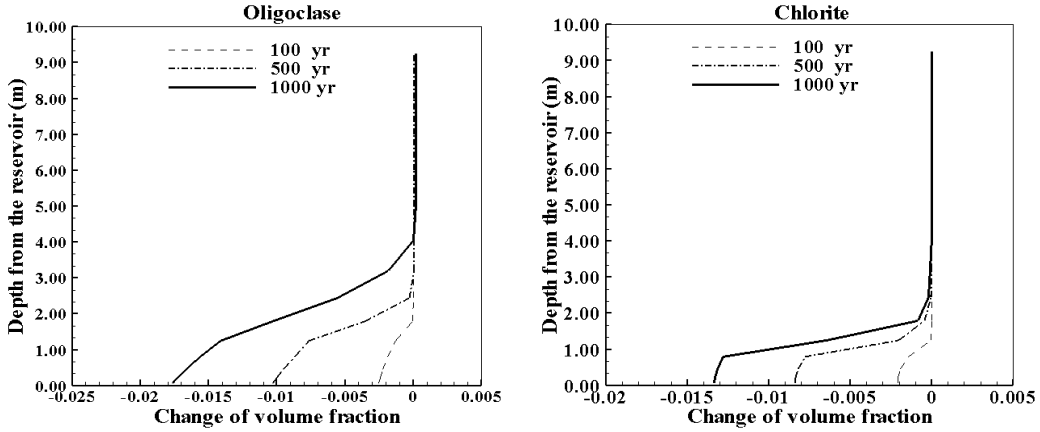


Figure 7. Percentage of amounts of CO_2 trapped in different phases over time for the 2-D radial model.



(a) Ankerite (b) Smectite-Na

Figure 8. Changes in volume fraction (with respect to total medium; positive values indicate precipitation, negative for dissolution) of ankerite and smectite-Na at different times obtained from the 1-D vertical column model.



(a) Oligoclase (b) Chlorite

Figure 9. Changes in volume fraction of oligoclase and chlorite at different times obtained from the 1-D vertical column model.

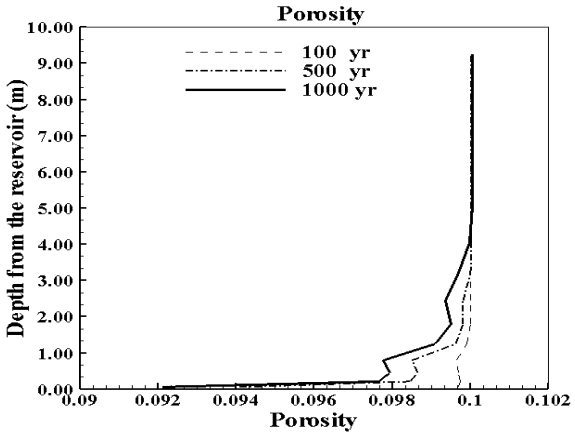
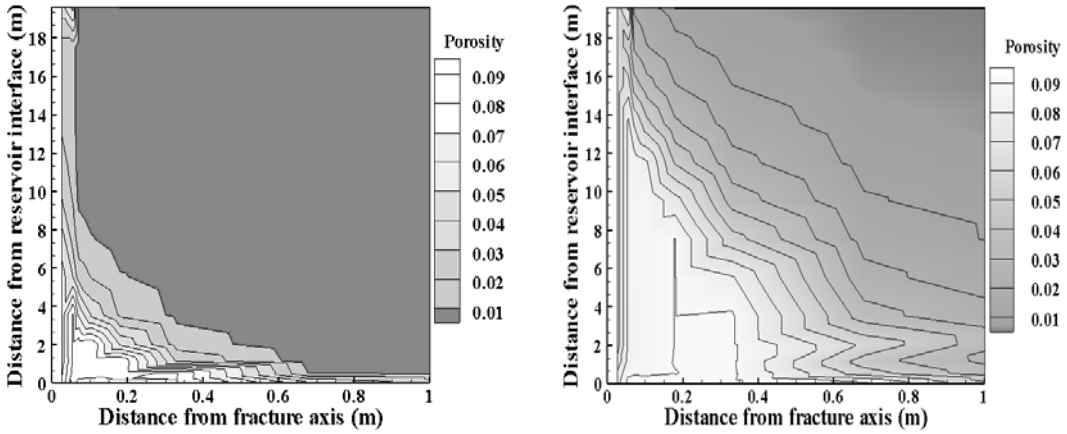


Figure 10. Porosity distribution at different times obtained from the 1-D vertical column model.



(a) 100 yr (b) 1000 yr

Figure 11. Porosity distribution after 100 and 1000 years obtained from the 2-D fractured caprock (shale) model.

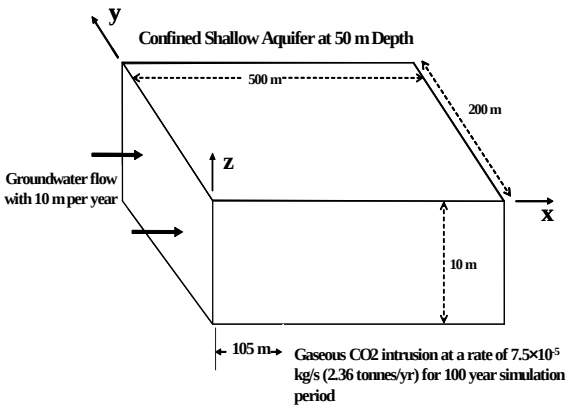


Figure 12. A schematic representation for the setup of reactive transport model.

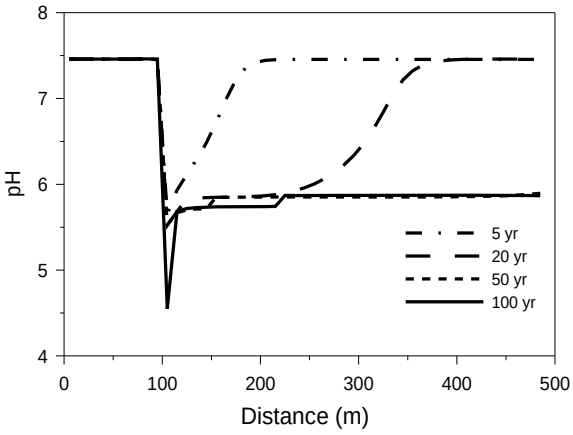


Figure 13. pH profiles (left) along the x-axis at y = 0 m at different times for St Peter sandstone.

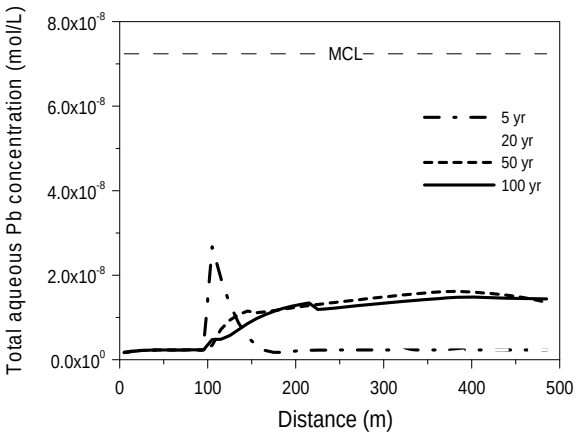


Figure 14. Total aqueous Pb concentration profiles (left) along x-axis at y = 0 m at different times for St Peter Sandstone.

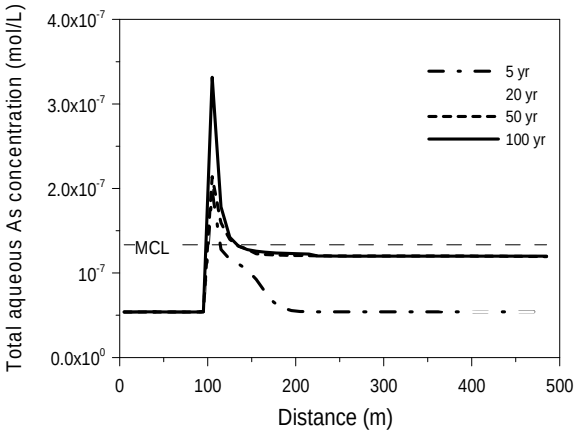


Figure 15. Total aqueous As concentration profiles (left) along x-axis at y = 0 m at different times for St Peter Sandstone

Table 1. Mineral volume fractions, possible secondary minerals, and kinetic properties for a St Peter Sandstone (the kinetic rates and surface areas were taken from Xu et al. (2006)).

Mineral	**Volume Fraction of solid**	**A (cm^2/g)**	**Parameters for Kinetic Rate Law**							
			Neutral Mechanism		**Acid Mechanism**			**Base Mechanism**		
			k_{25} ($mol/m^2/s$)	**E_a (KJ /mol)**	**k_{25}**	**E_a**	**$n(H^+)$**	**k_{25}**	**E_a**	**$n(H^+)$**
***Primary*:**										
Quartz	0.926778	9.8	1.023×10^{-14}	87.7						
K-feldspar	0.0505281	9.8	3.890×10^{-13}	38	8.710×10^{-11}	51.7	0.5	6.310×10^{-22}	94.1	-0.823
Oligoclase	0.00244551	9.8	1.445×10^{-12}	69.8	2.138×10^{-10}	65	0.457			
Kaolinite	0.00099595	1.95×10^{5}	6.918×10^{-14}	22.2	4.898×10^{-12}	65.9	0.777	8.913×10^{-18}	17.9	-0.472
Smectite-ca	0.0023423	5.64×10^{5}	1.660×10^{-13}	35	1.047×10^{-11}	23.6	0.34	3.020×10^{-17}	58.9	-0.4
Illite	0.00374012	6.68×10^{5}	1.660×10^{-13}	35	1.047×10^{-11}	23.6	0.34	3.020×10^{-17}	58.9	-0.4
Chlorite	0.00171185	9.8	3.02×10^{-13}	88	7.762×10^{-12}	88	0.5			
Kerogen-os	0.00238641	9.8	3.02×10^{-13}	88	7.762×10^{-12}	88	0.5			
Pyrite	0.000515	12.9	2.52×10^{-12}	62.76	2.34×10^{-7}	43.54	1			
dolomite	0.0045	12.9	2.52×10^{-12}	62.76	2.34×10^{-7}	43.54	1			
Calcite	0.00095337	Assumed at equilibrium								
Goethite	0.00060538	1.47×10^{5}	2.52×10^{-12}	62.76	2.34×10^{-7}	43.54	1			
Apatite	0.00220978	12.9			2.34×10^{-7}	43.54	1			
Barite	0.00016334	12.9			2.34×10^{-7}	43.54	1			
Arsenian pyrite	9.0594E-06	12.9			2.34×10^{-7}	43.54	1			
Greenockite	3.0363E-06	12.9			2.34×10^{-7}	43.54	1			
Cinnabar	1.4640E-08	12.9			2.34×10^{-7}	43.54	1			
Galena	7.8529E-06	12.9			2.34×10^{-7}	43.54	1			
Secondary:										
Dolomite		12.9	2.52×10^{-12}	62.76	2.34×10^{-7}	43.54	1			
Magnesite		9.8	4.571×10^{-10}	23.5	4.169×10^{-7}	14.4	1			
Ankerite		9.8	1.260×10^{-9}	62.76	6.457×10^{-4}	36.1	0.5			
Dawsonite		9.8	1.260×10^{-9}	62.76	6.457×10^{-4}	36.1	0.5			
Na-smectite		151.6	1.660×10^{-13}	35	1.047×10^{-11}	23.6	0.34	3.020×10^{-17}	58.9	-0.4
Pyromorphite		12.9			2.34×10^{-7}	43.54	1			
Ferroselite		12.9			2.34×10^{-7}	43.54	1			
Clausthalite		12.9			2.34×10^{-7}	43.54	1			

Table 2. Initial total aqueous concentration of major constituents obtained by initial equilibrium simulation for the base model.

Species	Concentration (mol/L)	Species	Concentration (mol/L)
Ca	1.9×10^{-3}	TIC	3.3×10^{-3}
Mg	4.2×10^{-5}	SO_4^{-2}	1.9×10^{-4}
Na	2×10^{-3}	Cl	2.1×10^{-4}
K	4.2×10^{-4}	Pb	1.3×10^{-9}
Fe	8.5×10^{-6}	As	5.4×10^{-8}
Si	6.4×10^{-4}	ionic strength	0.0085

Table 3. List of the need of reactive transport modeling on reliable reservoir and risk assessment for a CO2 sequestration project.

Modeling types	Issues solved
Reservoir modeling	Mineral alteration and CO_2 mineral trapping; Reservoir quality changes such as porosity and permeability; Storage of CO_2 in different phases (supercritical fluid, aqueous, and mineral), and variations with time.
Storage security	Caprock mineral alteration; Changes of caprock porosity, permeability, and capillary pressure behavior; Caprock sealing efficiency; Wellbore cement alteration
Impact of leakage on shallow aquifers	Groundwater quality changes induced by CO_2 itself because of dissolution and desorption of heavy metals (toxic compounds) bearing minerals and surface-sites. Impact of constituents carried with upward CO_2 migration from the storage such as organic matters.