Mineral alteration due to injection of CO_2, H_2S and SO_2 in deep arkosic formations

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ABSTRACT: Numerical modeling of geochemical processes is necessary to investigate long-term CO_2 injection in deep saline formations. We have developed a numerical model to investigate the fate of CO_2, H_2S and SO_2 in arkosic formations using hydrogeologic properties and mineral compositions characteristic of Texas Gulf Coast sediments. The simulations were performed using the reactive fluid flow and geochemical transport code, TOUGHREACT, to analyze mineral alteration and acid-gas sequestration.

1 INTRODUCTION

Numerical modeling of geochemical processes is necessary to investigate long-term CO_2 injection in deep saline formations, because aluminosilicate mineral alteration is very slow under ambient deep-aquifer conditions. Xu et al. (2003) performed reactive transport simulations of a 1-D radial well region under CO_2 injection conditions in order to analyze CO_2 immobilization through carbonate precipitation in Gulf Coast sandstones of the Frio formation of Texas. Sequestering less-pure CO_2 containing of H_2S and/or SO_2 requires less energy to separate from flue gas or a coal gasification process. Knauss et al. (2002) investigated the long-term impact of dissolved CO_2, H_2S and SO_2 using reactive transport simulations. Here we present simulations on mineral alteration, and consequent sequestration of CO_2, H_2S and SO_2 in a quartzose lithic arkose from the Gulf Coast Frio formation using a similar 1-D radial well region.

2 MODELING APPROACH

The non-isothermal reactive geochemical transport code TOUGHREACT (Xu & Pruess 2001) was developed by introducing reactive chemistry into the framework of the existing multi-phase fluid and heat flow code TOUGH2 (Pruess et al. 1999). Our modeling of flow and transport in geologic media is based on space discretization by means of integral finite differences. Full details on the numerical methods are given in Xu & Pruess (2001).

The simulator can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity, and can accommodate any number of chemical species present in liquid, gas and solid phases. A wide range of subsurface thermo-physical-chemical processes can be taken into account. Transport of aqueous and gaseous species by advection and molecular diffusion can be considered in both liquid and gas phases. Aqueous chemical speciation and gas dissolution and exsolution are assumed to be locally at equilibrium. Mineral dissolution and precipitation can be modeled subject to either local equilibrium or kinetic conditions. Changes in porosity and permeability are monitored from changes in mineral volume fractions without feedback to the fluid flow.

3 PROBLEM SETUP

The response of deep formations to CO_2, H_2S and SO_2 injection will depend on many factors, including formation permeability and porosity, and mineral composition. Before considering site-specific investigations, the general features and issues relating to the injection of acid gases into saline formation should be explored. The arkosic formation is assumed to be infinite and homogeneous with a thickness of 10 m, containing a 1 M saline fluid at a constant temperature of 75 ^{o}C (about 2 km depth). The well field is modeled as a circular region of 8000 m radius into which acid gases and water are injected. The injection scenarios and rates for each gas and water are given in Table 1. A total of four injection cases are considered. A 1-D radial grid was used with a spacing gradually increasing away from the well. Parameter specifications were chosen to be representative of conditions that may be encountered

in saline aquifers at a depths of about 2 km with a porosity of 0.3 and a permeability of 10^{-13} m^2. The injection was assumed to continue for a period of 100 years. The geochemical transport simulation was run for a period of 10,000 years.

Table 1. Injection rate (kg/s) of acid gases and water for each case.

Case	CO_2	Water	H_2S	SO_2
CO_2 only	1.0	0.5		
CO_2+H_2S	1.0	0.49	0.01	
CO_2+ SO_2	1.0	0.49		0.01
CO_2+H_2S+SO_2	1.0	0.49	0.005	0.005

The initial mineral composition (Table 2) was taken from the previous modeling study by Xu et al. (2003). The composition is a proxy for a quartzose lithic arkose from the Gulf Coast Frio formation, which is similar to those commonly encountered in sedimentary basins. Calcite and anhydrite were assumed to react at equilibrium. Other minerals were set to react under kinetic constraints. The kinetic parameters used are given in Xu et al. (2004). Prior to the reactive transport simulations, batch geochemical modeling of water-rock interaction was performed to obtain a nearly equilibrated water chemistry, using a pure 1.0 M NaCl solution reacting with the primary minerals listed in Table 2 at a temperature of 75 ^oC. The resulting water chemistry was used for the initial condition of reactive geochemical transport simulations.

Table 2. List of initial mineral volume fractions and possible secondary mineral phases.

Mineral	Chemical composition	Vol.%
***Primary*:**		
quartz	SiO_2	57.888
kaolinite	$Al_2Si_2O_5(OH)_4$	2.015
calcite	$CaCO_3$	1.929
illite	$K_{0.6}Mg_{0.25}Al_{1.8}(Al_{0.5}Si_{3.5}O_{10})(OH)_2$	0.954
kerogen-OS	$C_{64}H_{102}O_{40}S_{10}$	0.0
oligoclase	$CaNa_4Al_6Si_{14}O_{40}$	19.795
K-feldspar	$KAlSi_3O_8$	8.179
Na-smectite	$Na_{0.290}Mg_{0.26}Al_{1.77}Si_{3.97}O_{10}(OH)_2$	3.897
chlorite	$Mg_{2.5}$ $Fe_{2.5}Al_2Si_3O_{10}(OH)_8$	4.556
hematite	Fe_2O_3	0.497
***Secondary*:**		
anhydrite	$CaSO_4$	
magnesite	$MgCO_3$	
low-albite	$NaAlSi_3O_8$	
dolomite	$CaMg(CO_3)_2$	
siderite	$FeCO_3$	
Ca-smectite	$Ca_{0.145}Mg_{0.26}Al_{1.77}Si_{3.97}O_{10}(OH)$	
pyrite	FeS_2	
ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$	
dawsonite	$NaAlCO_3$ $(OH)_2$	
alunite	KAl_3 $(OH)_6(SO_4)_2$	

4 RESULTS

The fluid flow pattern is very similar for the four cases. Figure 1 shows water saturations versus radial distance. The reactive chemical modeling results obtained from the CO_2 only case are similar to those from CO_2 + H_2S. The results from CO_2 + SO_2 case are similar to those from CO_2 + SO_2 + H_2S. The results of CO_2 only and CO_2 + SO_2 injection cases will be presented here. A much lower pH (Fig. 2, about 0.6 close to the well region) was obtained from CO_2 + SO_2 injection. Corrosion and well abandonment is a significant issue. Anhydrite and alunite precipitation occur with SO_2 injection (Fig. 3). Minor pyrite forms with co-injection of H_2S or SO_2. Chlorite and oligoclase dissolution occurs in all four cases (Fig. 4). Significant CO_2 is trapped in ankerite (Fig. 5), dawsonite (Fig. 6), and some siderite. Total CO_2 sequestered in minerals is presented in Figure 7, and can reach 76 kg per cubic meter medium. CO_2 + SO_2 injection results in significant increases in porosity close to the well region (Fig. 8). More results on mineral alteration are reported in Xu et al. (2004).

5 CONCLUSIONS

Co-injection of SO_2 results in a larger and stronger acidic zone close to the well. Precipitation of CO_2 trapping minerals occurs in the higher pH ranges beyond acidic zones, whereas, SO_2 trapping minerals are stable in the low pH ranges (below 5) in the front of acidic zone. Corrosion and well abandonment caused by co-injection of SO_2 is a very significant issue. Significant CO_2 is sequestered in ankerite and dawsonite, and some in siderite. CO_2 mineral trapping capability can reach 76 kg per cubic meter medium. Most of SO_2 is trapped by alunite precipitation. Some SO_2 is trapped by anhydrite precipitation, and minor amount is pyrite. Addition of the acid gases and induced mineral alteration result in changes in porosity.

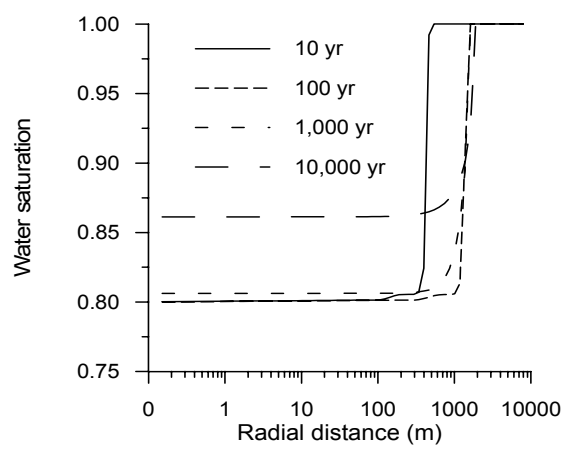
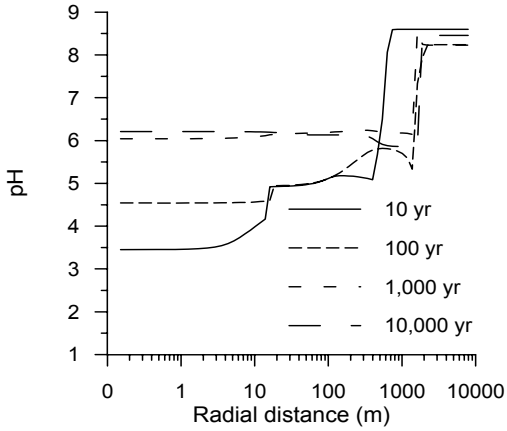
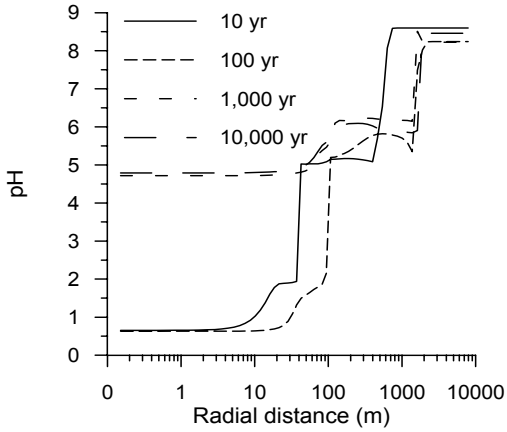


Figure 1. Water saturations at different times.

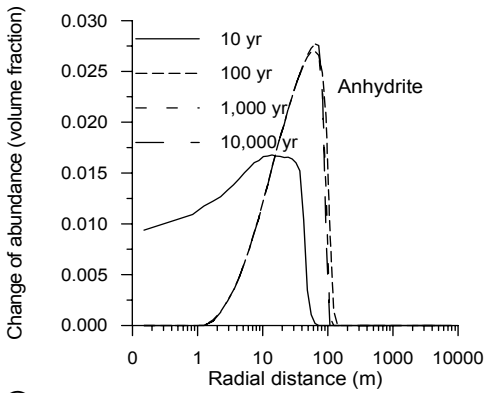


(a) CO_2



(b) CO_2+SO_2

Figure 2. pH at different times for the 1-D radial flow problem.



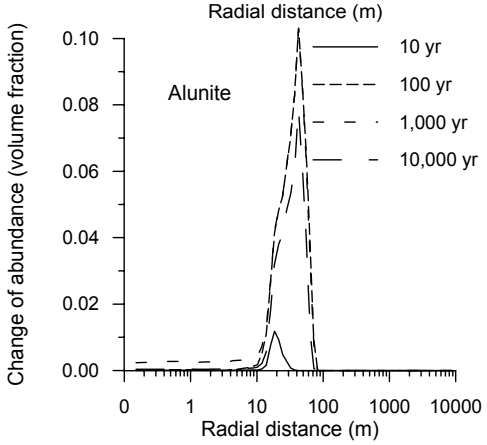


Figure 3. Change of anhydrite and pyrite abundance obtained from CO_2 + SO_2 case.

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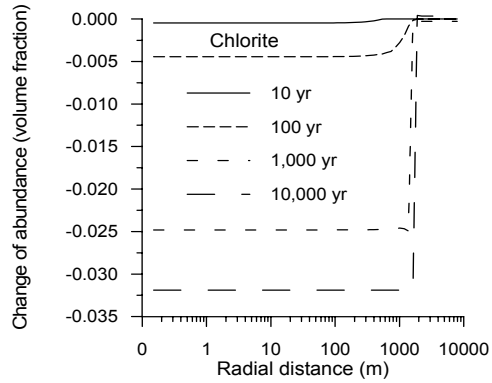


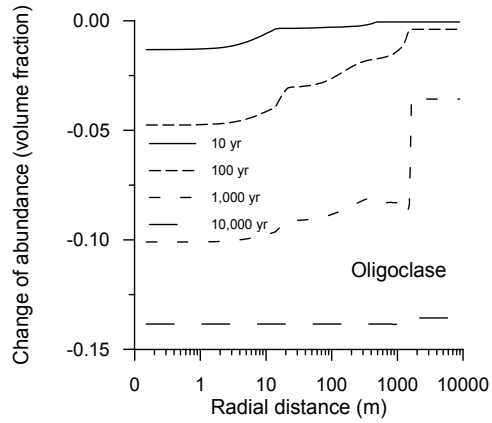
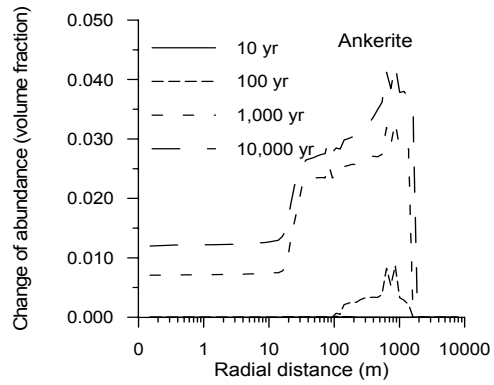
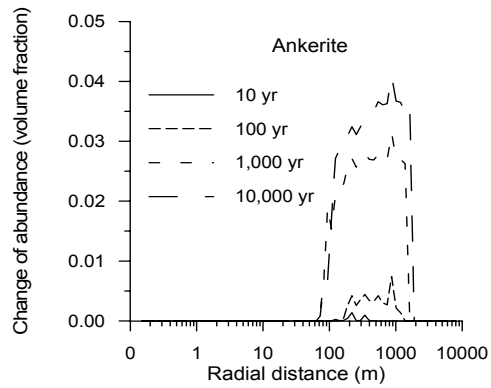


Figure 4. Change of chlorite and oligoclase abundance.

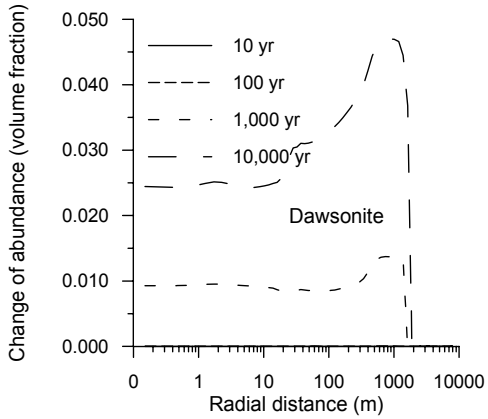


(a) CO_2

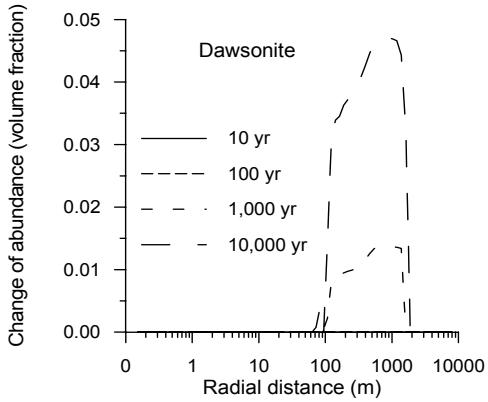


(b) CO_2+SO_2

Figure 5. Change of ankerite abundance.

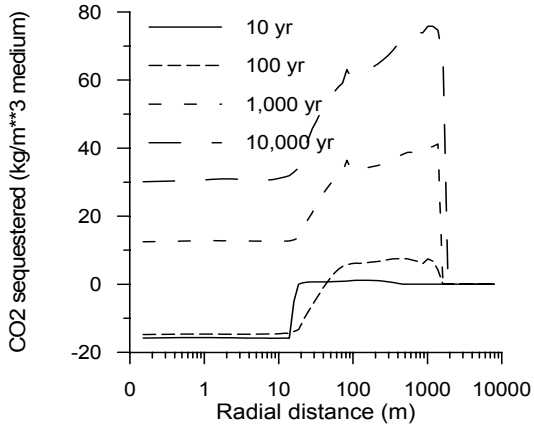


(a) CO_2

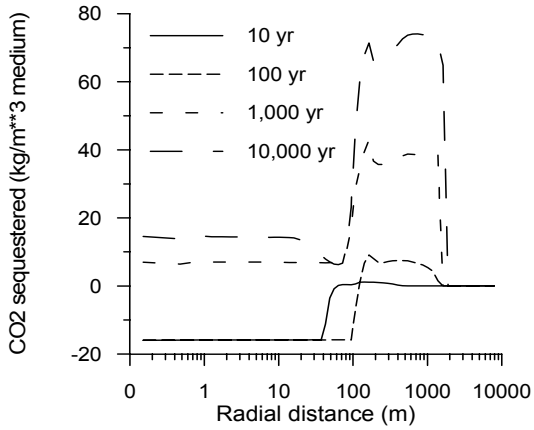


(b) CO_2+SO_2

Figure 6. Change of dawsonite abundance.



(a) CO_2



(b) CO_2+SO_2

Figure 7. Total CO_2 sequestered in mineral phases.

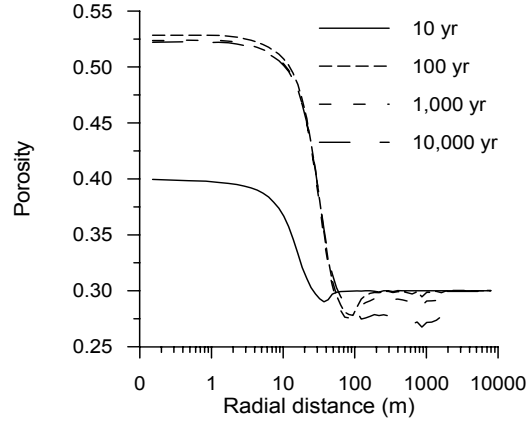


Figure 8. Porosity distribution from CO_2+SO_2 case.

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