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NUMERICAL STUDIES OF FLUID-ROCK INTERACTIONS IN ENHANCED GEOTHERMAL SYSTEMS (EGS) WITH CO_2 AS WORKING FLUID

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ABSTRACT

There is growing interest in the novel concept of operating Enhanced Geothermal Systems (EGS) with CO_2 instead of water as heat transmission fluid. Initial studies have suggested that CO_2 will achieve larger rates of heat extraction, and can offer geologic storage of carbon as an ancillary benefit. Fluid-rock interactions in EGS operated with CO_2 are expected to be vastly different in zones with an aqueous phase present, as compared to the central reservoir zone with anhydrous supercritical CO_2. Our numerical simulations of chemically reactive transport show a combination of mineral dissolution and precipitation effects in the peripheral zone of the systems. These could impact reservoir growth and longevity, with important ramifications for sustaining energy recovery, for estimating CO_2 loss rates, and for figuring tradeoffs between power generation and geologic storage of CO_2.

INTRODUCTION

The U.S. Department of Energy has broadly defined Enhanced (or Engineered) Geothermal Systems (EGS) as engineered reservoirs that have been created to extract economical amounts of heat from geothermal resources of low permeability and/or porosity (MIT, 2006). The MIT report indicated that EGS could become a major supplier of primary energy for U.S. base-load generation capacity by 2050. Here we consider a novel EGS concept that would use carbon dioxide (CO_2) instead of water as heat transmission fluid, and would achieve geologic sequestration of CO_2 as an ancillary benefit (Brown, 2000).

Numerical simulations of fluid dynamics and heat transfer indicate that CO_2 is superior to water in its ability to mine heat from hot fractured rock (Pruess, 2006). Carbon dioxide also offers advantages with respect to wellbore hydraulics, in that its larger compressibility and expansivity as compared to water would increase buoyancy forces and reduce the parasitic power consumption of the fluid circulation system. While the thermal and hydraulic aspects of a CO_2-EGS system look promising, major uncertainties remain with regard to chemical interactions between fluids and rocks.

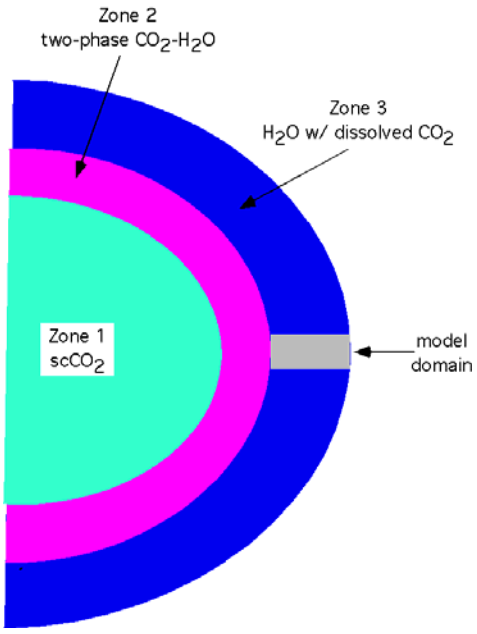

Figure. 1. Schematic showing portions of the three zones with different phase compositions in an EGS operated with CO_2. The model domain studied in this paper is in the single-phase Zone 3, extending from the two-phase Zone 2 on the left to the outer boundary of the EGS on the right."sc" stands for supercritical CO_2.

As shown in Figure 1, a fully developed EGS with CO_2 would consist of three distinct zones (Fouillac et al., 2004; Ueda et al., 2005), (1) a central zone or

"core" (Zone 1) in which all aqueous phase has been removed by dissolution into the flowing CO_2 stream, so that the reservoir fluid is a single supercritical CO_2 phase; (2) a surrounding intermediate zone (Zone 2), in which the reservoir fluid consists of a two-phase water-CO_2 mixture; and (3) an outer or peripheral zone (Zone 3), in which the reservoir fluid is a single aqueous phase with dissolved CO_2.

Geochemical processes are expected to be quite different in the three zones. The absence of water in the inner (core) zone poses unique questions, as little is presently known about the geochemistry of non-aqueous systems. The aqueous fluids initially present in an EGS reservoir would be quickly removed by immiscible displacement by the CO_2, and by dissolution (evaporation) into the flowing CO_2 stream. Continuous operation of a CO_2-EGS may produce a rather dry CO_2 stream. Research on reactions between supercritical CO_2 and rocks in the absence of water has started only recently (Regnault et al., 2005). Carbon dioxide is not an ionic solvent, which would reduce the potential for dissolution and subsequent re-precipitation of minerals, and avoid problems of scaling and formation plugging (Brown, 2000). It appears likely that prolonged exposure to supercritical CO_2 will cause dehydration reactions that would remove loosely bound water from rock minerals. Such reactions may reduce the molar volume of the minerals involved, which would increase porosity and permeability of the formations, and might promote reservoir growth (Pruess, 2006).

Rock-fluid interactions in Zones 2 and 3 would be mediated by the aqueous phase. Some information on relevant processes is available from laboratory experiments (Ueda et al., 2005), natural CO_2-bearing geothermal systems (Giolito et al., 2007), and reactive chemical transport modeling (André et al., 2007; Gherardi et al., 2007). The peripheral zone (Zone 3) of an EGS operated with CO_2 may experience a combination of mineral dissolution and precipitation effects that could impact reservoir growth and longevity. The long-term behavior of this outermost zone will be crucial for sustaining energy recovery, for estimating CO_2 loss rates, and for figuring tradeoffs between power generation and geologic storage of CO_2. We have performed reactive transport simulations to study CO_2-induced mineral alteration in the outer zone, associated changes in reservoir porosity, and sequestration of CO_2 by secondary carbonate precipitation.

PROBLEM SETUP

Geometric and Flow Conditions

Before moving into site-specific investigations, general CO_2-EGS features and issues should be explored. This can be done by abstracting site-specific features and thereby attempt to represent characteristics that may be common to many of these systems. Basic issues are the physical and chemical changes induced by dissolved CO_2, including dissolution of primary minerals, formation of secondary minerals, CO_2 mineral trapping, and changes in reservoir porosity and permeability.

As pointed out by Gherardi et al. (2007), when interactions between CO_2-rich fluid and rocks occur under fully liquid-saturated conditions and a diffusion-controlled regime, pH will be buffered at higher values, favoring carbonate precipitation that leads to further sealing of the caprock of the CO_2 storage reservoir. Even though their simulations were performed for a low temperature of 45 ^oC, the peripheral zone in a higher temperature CO_2-EGS reservoir may show similar trends. In the simulations presented here, we used a one-dimensional model (Figure 1). At the left boundary of the model domain, water chemical composition was specified by equilibrating with a high CO_2 pressure and primary mineral assemblage (see below), to represent the single-aqueous-phase peripheral zone of a CO_2-EGS reservoir. The right boundary is closed for water flow and chemical transport. The 1-D linear flow model allows us to identify the geochemical parameters and controls that have the most sensitive influence on reservoir behavior. The geometric and hydrogeologic specifications of the 1-D flow problem are given in Table 1. The simulation was performed under an isothermal condition of 200 ^oC. Temperature and pressure at the left and right boundaries are set to be constants throughout the simulation and equal to their initial values, or 200 ^oC and 500 bar. Therefore, advection would occur only in response to pressure changes from dissolution and precipitation reactions.

Table 1. Geometric and hydrogeologic specifications for 1-D linear flow problem.

Geometric variables:	
Length of the column	12 m
Gridding	60 x 0.2 m
Cross-section area	1 m^2
Reservoir properties:	
Permeability	1×10^{-13} m^2
Porosity	10 %
Rock grain density	2600 kg/m^3
Rock specific heat	920 $J/kg/^oC$
Thermal conductivity	2.51 $W/m/^oC$
Initial and boundary conditions:	
Pressure	500 bar
Temperature	200 ^oC
Aqueous transport:	
Tortuosity	0.46
Aqueous diffusion coefficient	1×10^{-9} m^2/s

Mineralogical Composition and Reaction Kinetics

The present study is not intended to represent any particular site. However, data for mineralogical composition were taken from the European Hot Dry Rock research site (HDR, Soultz project), which is situated at Soultz-sous-Forêts, northern Alsace, France (Jacquot, 2000; Durst, 2002; Bächler, 2003; André et al., 2006). The Soutz reservoir is composed of altered granite blocks partly cemented by alteration products that consist essentially of clay minerals and carbonates (see Table 2). As the primary minerals initially present in the rock matrix dissolve due to CO_2 intrusion, some secondary carbonate minerals (siderite, ankerite and dawsonite) may be formed; all these minerals were included in the simulation. Mineral dissolution and precipitation are considered under kinetic constraints. A general kinetic rate expression is considered, which is based on transition state theory (Lasaga et al., 1994). The parameters used are taken from Xu et al. (2006).

Table 2. List of initial mineral volume fractions in altered granite from Soultz (Jacquot, 2000; Durst, 2002; Bächler, 2003) and potential secondary mineral phases (with zero volume fractions).

Mineral	*Volume fraction in term of solid*	*Specific surface area A (cm^2/g)*
Primary**:**		
Quartz	0.0409	9.8
Calcite	0.033	9.8
K-feldspar	0.139	9.8
Chlorite	0.048	108.7
Dolomite	0.008	9.8
Na-smectite	0.07469	108.7
Ca-smectite	0.02231	108.7
Pyrite	0.007	12.9
Illite	0.246	108.7
Non-reactive	0.3681	
Secondary**:**		
Amorphous silica (precipitation)		9.8
Siderite		9.8
Ankerite		9.8
Dawsonite		9.8

Water Chemistry

We started with a 165 ^oC water sample taken from Soultz Well CPK1 at 3500 m depth. Initial water chemistry in the porous medium column was obtained by equilibrating the measured water composition with their corresponding primary mineral assemblage (Table 2) at a temperature of 200 ^oC. The resulting initial water composition is shown in Table 3. The important boundary parameter controlling rock-fluid interactions is the aqueous concentration of CO_2. At the left boundary, we applied a water that was obtained by equilibrating the initial water with a CO_2 partial pressure of 350 bar. The resulting chemical composition of the boundary water is also given in Table 3.

Table 3. List of chemical compositions (units are mol/kg H_2O except for pH) of initial and boundary waters used in the simulation, which were derived from a Soultz Well GPK1 sample (Durst, 2002).

Water type	Initial water	Boundary water
Chemical components	Equilibrium with the minerals (200^oC)	
Ca	1.705×10^{-1}	2.122×10^{-1}
Mg	5.536×10^{-3}	6.949×10^{-3}
Na	1.211	1.147
K	9.432×10^{-2}	3.178×10^{-2}
Fe	1.981×10^{-7}	8.792×10^{-3}
Cl	1.719	1.686
SiO_2(aq)	4.131×10^{-3}	3.758×10^{-3}
Total CO_2(aq)	**1.724×10^{-3}**	**1.071**
SO_4	2.391×10^{-3}	1.990×10^{-3}
Al	1.519×10^{-6}	1.113×10^{-6}
pH	**5.7**	**4.2**

Simulation Tool

The simulations employed the non-isothermal reactive geochemical transport code TOUGHREACT (Xu et al., 2006); which introduces reactive chemistry into the multiphase fluid and heat flow code TOUGH2 (Pruess, 2004). More information on the TOUGHREACT can be found at http://www-esd.lbl.gov/TOUGHREACT/.

Temporal changes in reservoir rock porosity and permeability due to mineral dissolution and precipitation can modify fluid flow path characteristics. This feedback between flow and chemistry is considered in our model. Changes in porosity are calculated from variations in mineral volume fractions. A simple cubic Kozeny-Carman grain model was used in the current problem

$$\frac{k}{k_0} = \left(\frac{\phi}{\phi_0}\right)^3 \left(\frac{1-\phi_0}{1-\phi}\right)^2 \qquad (1)$$

where ϕ is the porosity, k is the permeability (in m^2), and subscripts 0 denote initial variable values. A broad range of subsurface thermal-physical-chemical processes are considered under various

thermohydrological and geochemical conditions of pressure, temperature, water saturation, ionic strength, pH and Eh. Further details on the process capabilities of the TOUGHREACT code are given in Xu et al. (2006)

RESULTS AND DISCUSSION

The pH distribution along the column is presented in Figure 2. The initial value throughtout the column is close to 6. The pH close to the left boundary has a value of 4.5, higher than at the boundary (4.2; see Table 3), which is buffered by mineral assemblage. The pH evolution is caused by both transport and reactions. Distribution of conservative tracer concentrations is presented in Figure 3, to illustrate transport contribution.

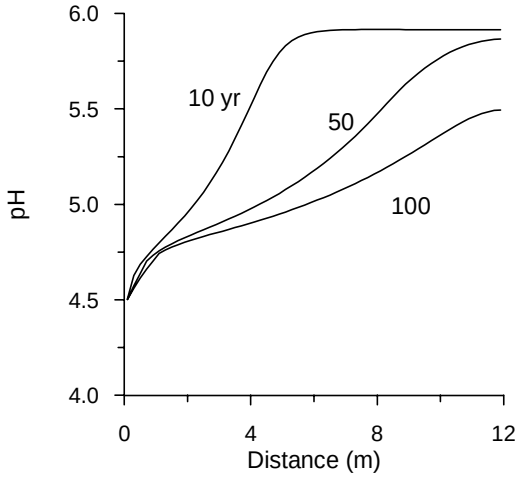

Figure. 2. pH distribution at different times obtained from the 1-D problem using a Soultz mineralogy. The left of the model domain (see Figure 1) is at x = 0 m.

The total dissolved CO_2 concentrations, including CO_2(aq) and associated aqueous species such as HCO_3^-, CO_3^{2-}, $CaHCO_3^+$, $MgHCO_3^+$, and $FeHCO_3^+$, are presented in Figure 4. The total CO_2 concentration close to the left boundary has a value of 1.2 mol/kg, which is somewhat larger than in the boundary water (in Table 3, boundary value is 1.07 mol/kg H_2O). This is because precipitation of the secondary clay minerals smectite and illite consumes H_2O (hydro-ration) which was considered in our geochemistry model.

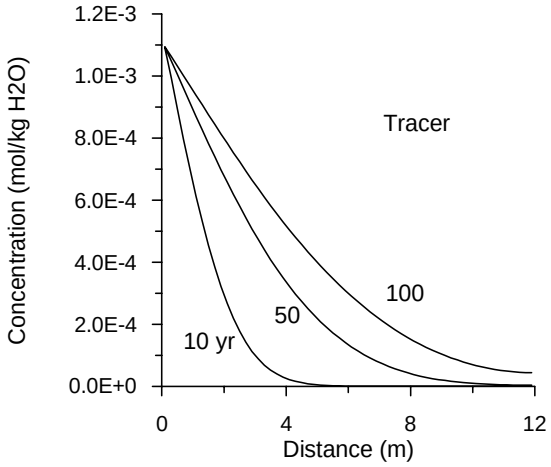

Figure 3. Concentrations of a conservative solute tracer at different times.

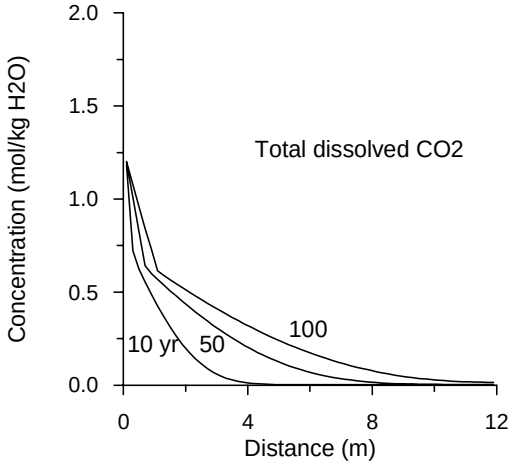

Figure 4. Distribution of total CO_2(aq) concentrations at different times.

The lowered pH due to the intrusion of CO_2-rich water induces dissolution of primary minerals such as calcite, K-feldspar, and chlorite, and precipitation of secondary carbonate and clay minerals such as siderite, dolomite, smectite and illite. Consequently, porosity decreases significantly close to the left boundary (Figure 5), because (1) CO_2-rich water adds solute mass to the rock matrix and (2) molar volumes of secondary clays are larger than those of the primary minerals. The extent of porosity change is consistent with the mineral alteration mentioned above. The porosity was reduced up to 0.094, from the initial value of 0.1.

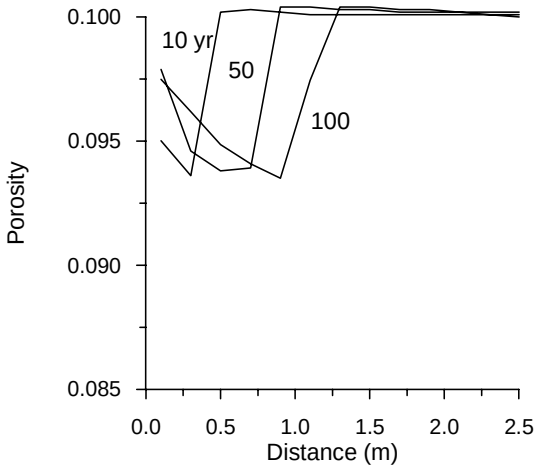

Figure 5. Profiles of porosity at different times.

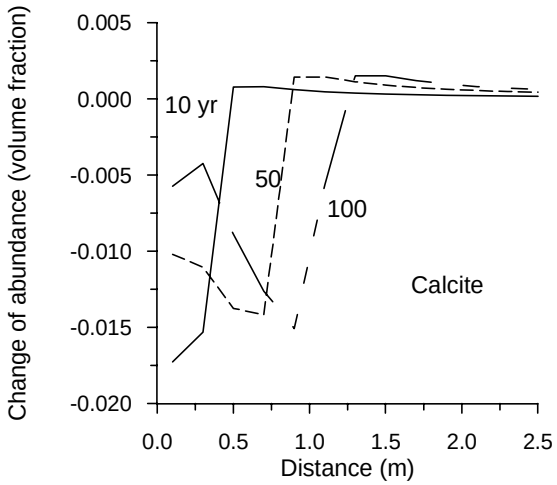

Figure 6. Changes of calcite abundance (in volume fraction in terms of porous medium; positive values indicate precipitation and negative dissolution) along the distance at different times.

Although calcite was initially present in the rocks, it generally dissolves due to the low pH. The calcite dissolution front moves with time (Figure 6). K-feldspar dissolution occurs close to the CO_2 source and gradually decreases away from it (Figure 7). As primary minerals dissolve, secondary carbonate and clay minerals are formed. Chlorite (Figure 8) dissolves and supplies Mg and Fe to induce dolomite (Figure 9) and siderite (Figure 10) precipitation.

The precipitation fronts of dolomite and siderite move with time, coinciding with the fronts of dissolution of calcite (Figure 6) and chlorite (Figure 8). Precipitation of clay minerals (smectite-Na, smectite-Ca, and illite) was observed in the simulation; only that of smectite-Na is presented in Figure 11. Precipitation of dolomite and siderite sequesters a significant amount of CO_2 (Figure 12). A maximum of about 50 kg CO_2 per m^3 of medium was trapped by carbonate precipitation.

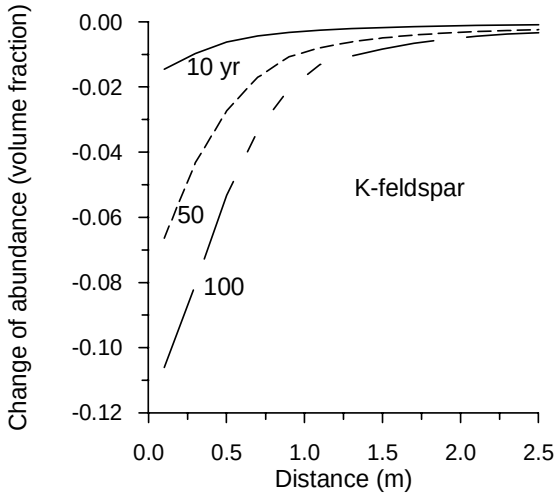

Figure 7. Changes of K-feldspar abundance along the column at different times.

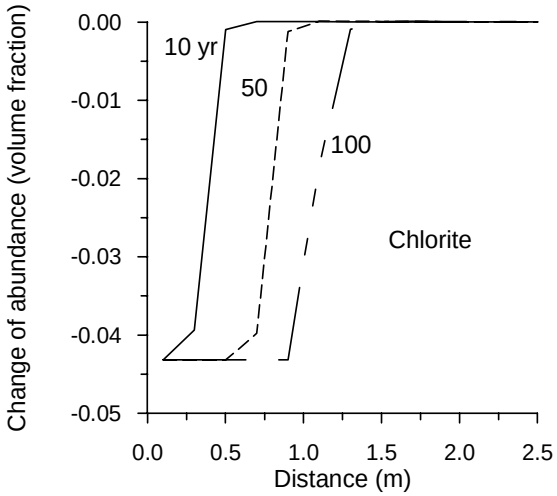

Figure 8. Changes of chlorite abundance along the column at different times.

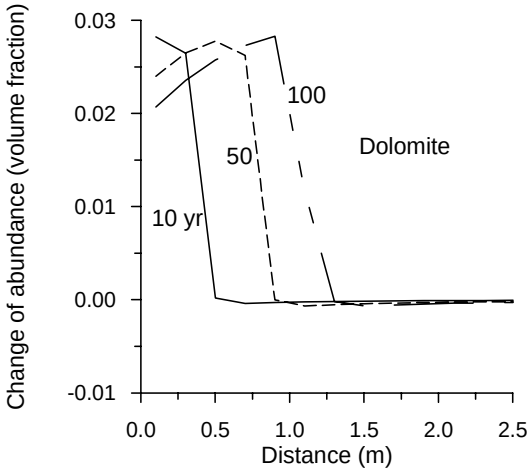

Figure 9. Changes of dolomite abundance along the column at different times.

In the previous simulation, we considered dolomite precipitation, which under field conditions tends to be kinetically inhibited. To evaluate the impact on mineral alteration, porosity change, and CO_2 mineral trapping when dolomite precipitation is disregarded, we performed an additional simulation. In this case, ankerite precipitation occurs because of Mg surplus without consumption by dolomite precipitation. Siderite precipitation still occurs, but the amount is smaller. The extent of porosity change is slightly smaller (compare Figures 5 and 13). The zone of CO_2 trapped (Figure 14) by ankerite and siderite precipitation is slightly narrower (compare Figures 12 and 14), but the maximum of CO_2 mineral trapping is similar (50 kg/m^3 medium).

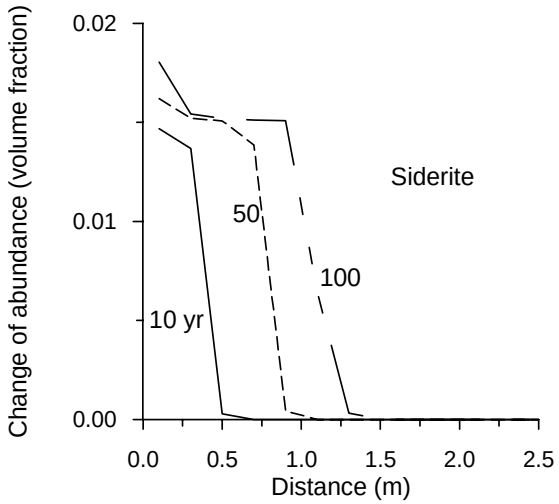

Figure 10. Changes of siderite abundance along the column at different times.

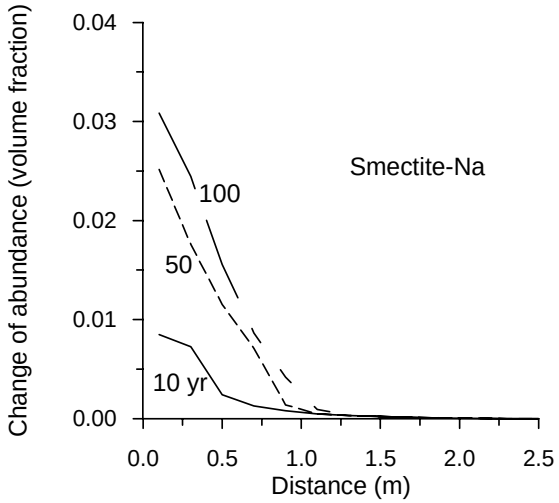

Figure 11. Changes of smectite-Na abundance along the column at different times.

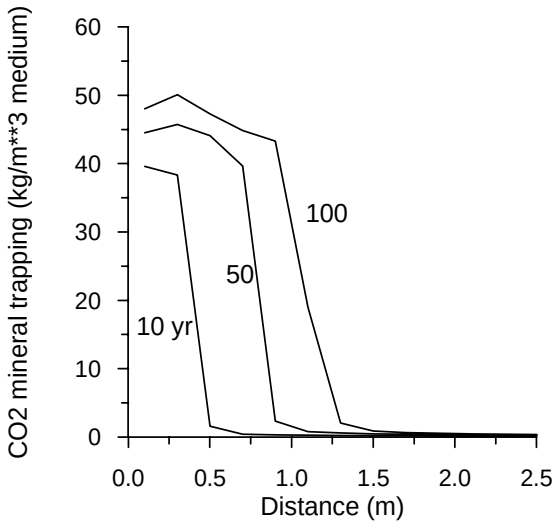

Figure 12. Cumulative amounts of CO_2 sequestered by secondary carbonate precipitation along the column at different times.

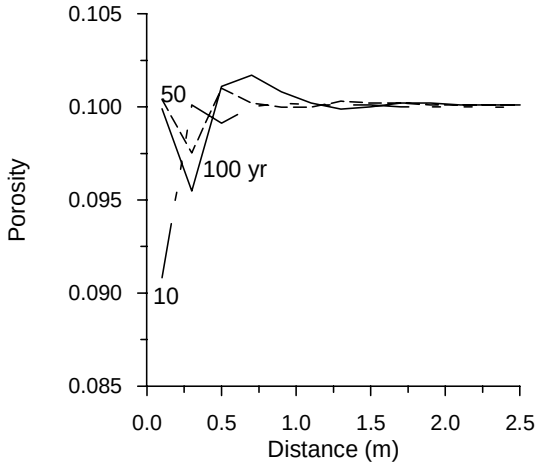

Figure 13. Distribution of porosity along the column at different times obtained from the additional simulation without considering dolomite precipitation.

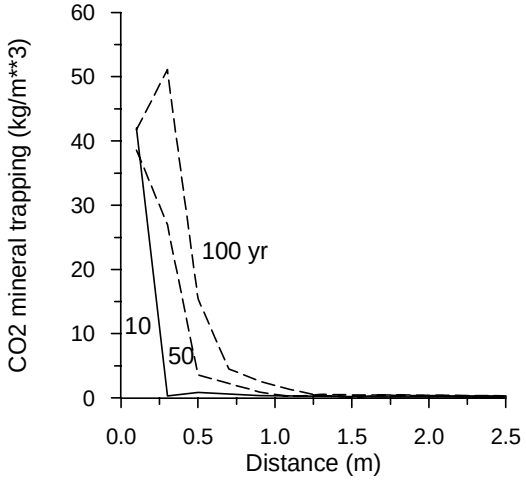

Figure 14. Cumulative amounts of CO_2 sequestered by secondary carbonate precipitation at different times obtained from the additional simulation.

CONCLUSIONS AND RECOMMENDATIONS

We have developed a one-dimensional model for the peripheral zone of a CO_2-EGS system using the mineralogical composition and water chemistry from the Soultz EGS site. Major findings from our simulation are:

- Dissolved CO_2 may diffuse to the peripheral zone of the EGS and induce dissolution of primary minerals and precipitation of secondary carbonate and clay minerals. For Soultz mineralogy, the main dissolving minerals are calcite, K-feldspar, and chlorite. Major precipitating secondary carbonates are dolomite, siderite and ankerite, and clay minerals are Na-smectite, Ca-smectite and illite.
- The transport of dissolved CO_2 and mineral alteration generally decreases porosity, which could result in the formation of a lower permeable barrier that would impact reservoir growth and longevity. Significant CO_2 could be fixed through precipitation of carbonate minerals, which can offer geologic storage of carbon as an ancillary benefit.

The time frame to form a lower permeable barrier and the fixation of CO_2 is a function of reaction kinetics of mineral dissolution and precipitation, which requires further study. The extent of porosity decrease and amount of CO_2 mineral trapping depends on the primary mineral composition.

Sensitivity studies on different rock mineralogies should be performed in the future. Using natural analogues of high-pressure CO_2 reservoirs, refinements on thermodynamic, kinetic and physical data should be useful. Reactivity between supercritical CO_2 and rock is not well understood. Experimental studies are required to quantitatively describe the reaction kinetics. Investigations on chemical changes for the entire reservoir domain should be addressed in the future.

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