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EXPERIMENT-BASED MODELING OF GEOCHEMICAL INTERACTIONS IN CO_2-BASED GEOTHERMAL SYSTEMS

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ABSTRACT

Carbon dioxide (CO_2) has recently been considered as an alternative geothermal working fluid because of some favorable fluid dynamics and heat transfer properties compared to water. While the thermal and hydraulic aspects of CO_2-based geothermal systems look promising, major uncertainties remain with regard to chemical interactions between fluids and rocks, particularly during the transition from resident water to supercritical CO_2. We have performed reactive transport modeling to study fluid-rock interactions and its impact on porosity and permeability changes, based on batch experiments with rock and mineral samples and mixtures of water and CO_2; these experiments are conducted at temperature and pressure conditions that are representative of typical geothermal systems. Different thermodynamic databases are tested, and the geochemical model is calibrated by adjusting the reactive surface area, as a representative rate controlling parameter, to fit the experimental data of mineral dissolution. The flow and geological conditions of a CO_2 geological sequestration site at Cranfield, Mississippi are used for the modeling analyses. The objective of this research is to (1) investigate mineral dissolution and precipitation patterns, (2) evaluate associated porosity changes and effects on fluid and heat transfer, and (3) determine thermodynamic and kinetic reaction rate parameters that can be used to constrain coupled process models.

INTRODUCTION

As part of an effort to reduce atmospheric emissions of carbon dioxide (CO_2), a novel concept of operating enhanced geothermal system (EGS) using CO_2 instead of water as working fluid (CO_2-EGS) and achieving simultaneous geologic sequestration of CO_2 has been proposed and evaluated (Brown, 2000; Pruess, 2006 and 2008). CO_2 appears to be superior to water in extracting heat from hot fractured rock and reducing the power consumption of the fluid circulation system, because its large expansivity and lower viscosity result in substantially greater mass flow rates than those of water.

In recent years, a similar concept, a so-called CO_2-plume geothermal (CPG) system, has been proposed (Randolph and Saar, 2011). The CPG system utilizes existing, naturally porous, high-permeability geologic formations (reservoirs) for geothermal energy recovery. The major benefit of the CPG system over the EGS is that the CPG system does not require hydrofracking, which helps increase fracture permeability but may induce seismicity.

While the thermal and hydraulic aspects of these CO_2-based geothermal systems look promising, major uncertainties remain with regard to chemical interactions between fluids and rocks, particularly during the transition from resident water to supercritical CO_2. Several experimental and reactive transport modeling studies have been conducted, but the effort to validate the thermodynamic and kinetic data is very limited (e.g., Aradóttir et al., 2012a and b; Lo Ré et al., 2012).

We are currently developing in collaboration with Palo Alto Research Center (PARC) an experiment-based geochemical model capable of simulating CO_2-based geothermal systems both during the transition from water to supercritical CO_2 and throughout the subsequent long-term operation. For this purpose,

PARC has built an automated multichannel reactor system and conducted batch and flow-through kinetic experiments with rock and mineral samples and mixtures of water and CO_2 at various conditions. In this paper, we briefly review the experimental setup and data, and discuss the applicability of available thermodynamic databases to the tested system and the results of the geochemical model calibration to the batch experimental data of mineral dissolution. Then, an application example of the calibrated model is presented for studying fluid-rock interactions and its impact on porosity and permeability changes in a CFG system.

EXPERIMENTAL SETUP AND DATA REVIEW

Petro et al. (2012) have developed an integrated multichannel reactor system for evaluation of geothermal rock-fluid interactions, which can be operated over a wide range of high-pressure (up to 300 bar) and high-temperature (up to 300 °C) conditions. The system is coupled to an on-line diagnostics system for real-time complex ion analysis under the reaction/interaction conditions. Therefore, it is capable of producing data on temporal changes of dissolved ion concentrations throughout the course of an experiment, which are used to estimate thermodynamic and kinetic parameters associated with dissolution of each mineral for a specific set of experimental conditions. The recent system upgrade has included a flow-through circulation channel, which allows us to further examine additional factors related to the complex interaction kinetics (Petro et al., 2013).

Among kinetic dissolution data of various minerals generated by PARC, in this study we discuss the results of calcite, dolomite, chlorite, labradorite, and illite, which are relevant to the application example discussed in the later section on reactive transport modeling of CO_2-based geothermal systems. The pressure of the batch reactor is maintained at 82.7 bar, and two temperature conditions (120 °C and 150 °C) are tested. More details of the experimental data can be found in Petro et al. (2012, 2013).

MODELING APPROACH TO INTERPRETING GEOCHEMICAL REACTION

Using the same experimental pressure and temperature conditions, we perform TOUGHREACT numerical modeling analyses (Xu et al., 2011) for some specific minerals selected, and compare the simulation results with measured data. A new fluid property module, based on Spycher and Pruess (2010), is used. This module provides an accurate description of the thermophysical properties of mixtures of water and CO_2 under conditions typically encountered in CO_2-water systems of interest (12°C ≤ T ≤ 250°C; 1 bar < P ≤ 600 bar).

A general form of rate expression is used in the TOUGHREACT program, which is based on transition state theory (Lasaga et al., 1994; Steefel and Lasaga, 1994):

$$r = kA\left[1-\left(\frac{Q}{K}\right)^{\theta}\right]^{\eta} \qquad (1)$$

where r is the rate of dissolution/precipitation, k is the temperature dependent rate constant, A is the specific reactive surface area, K is the equilibrium constant for the mineral dissolution/precipitation reaction, and Q is the reaction quotient. The parameters θ and η must be determined from experiments, but they are often taken equal to one. Positive values of r indicate dissolution and negative values precipitation.

For the kinetic rate constant k, in addition to the mechanism at neutral pH, we also consider acid or base mechanisms, which are catalyzed by H^+ or OH^-, respectively. The inclusion of the acid mechanism is particularly important in this study since the pH of the CO_2-saturated water is acidic.

While the mineral dissolution rate is represented by the product of the kinetic-rate constant and the reactive surface area as shown in Eq. (1), it is not possible to independently estimate both parameters using the profile of dissolved ion concentrations only. Therefore, as a representative rate controlling parameter, the reactive surface area is estimated to fit the experimental data. It should also be noted that the equilibrium constant K is an important parameter not only affecting the dissolution rate but also the solubility of minerals, and that log(K) values for mineral dissolution can vary considerably depending on thermodynamic databases. However, with the current experimental setup, it is not possible to ensure consistency of log(K) data relevant to dissolution of a certain mineral by only updating the thermodynamic data of the mineral of interest at a given condition. Therefore, although the match between the measured and the modeled ion concentrations may not be satisfactory due to the lower solubility of the model than the measured one, no attempt is made to calibrate log(K) values in this study. The parameters used for calculating the kinetic-rate constant are obtained from Palandri and Kharaka (2004) and Steefel (2001). Most solubility products for minerals and aqueous equilibrium constants are taken from the database used with EQ3/6 V7.2b (Wolery, 1992), which we will refer as the EQ3/6 database, and thermodynamic data from Arnorsson and Stefánsson

(1999) are used for andesine, a plagioclase feldspar, whose composition is fairly close to that used in the experiment (labradorite).

For geochemical parameter estimation using the available experimental data, we use iTOUGH2-PEST (Finsterle, 2011), a universal optimization code for generic forward models. iTOUGH2-PEST inherits all the capabilities of iTOUGH2 (Finsterle, 2007) as a computer program for parameter estimation, sensitivity analysis, and uncertainty propagation analysis, and uses the PEST protocol (Doherty, 2007, 2008) as a way to communicate between application models and iTOUGH2. iTOUGH2 was originally developed for use with the TOUGH2 forward simulator for nonisothermal flows of multiphase, multicomponent fluids (Pruess, 1999). However, with the iTOUGH2-PEST module, iTOUGH2 can be used as a universal optimization code for non-TOUGH2 models.

RESULTS OF MODEL CALIBRATION

Effect of Thermodynamic Data on Mineral Dissolution Rate and Solubility

Due to the scarcity of raw data, regression and extrapolation of available thermodynamic data is required to create a thermodynamic database (Oelkers et al., 2009). As a consequence, the uncertainty implicit in thermodynamic data cannot be avoided. While many of the thermodynamic data for mineral solubility and solute speciation may be similar in different databases, some major discrepancies can exist for several minerals. Therefore, even if the kinetic rate constant and the reactive surface area are kept unchanged, the dissolution profile of a certain mineral can significantly differ depending on the thermodynamic database used for simulation.

We explore the effect of using different thermodynamic databases on simulation of mineral dissolution. Among currently available and widely used databases, the EQ3/6, SOLTHERM (Reed and Palandri, 2006), and THERMODDEM (Blanc et al., 2009) databases are compared for calcite and illite dissolution reactions. As shown in Fig. 1a, while the agreement between the measurements and any model predictions for calcite dissolution might be acceptable at early times, the difference is significant at late times. That is, for appropriate model validation, it might be critical to conduct kinetic experiments for a sufficiently long period (i.e., until reaching quasi-equilibrium state). Even in the case of illite, only one among the thermodynamic databases tested is able to reasonably reproduce the dissolution profile (see Fig. 1b). Therefore, model validation might be the essential prerequisite for successful geochemical reactive transport modeling, particularly for geothermal systems with high temperature and high pressure where data for dissolution rate and solubility data are scarce. Based on this result, the EQ3/6 thermodynamic database is used for the rest of simulations, except for the calibration of labradorite dissolution reaction.

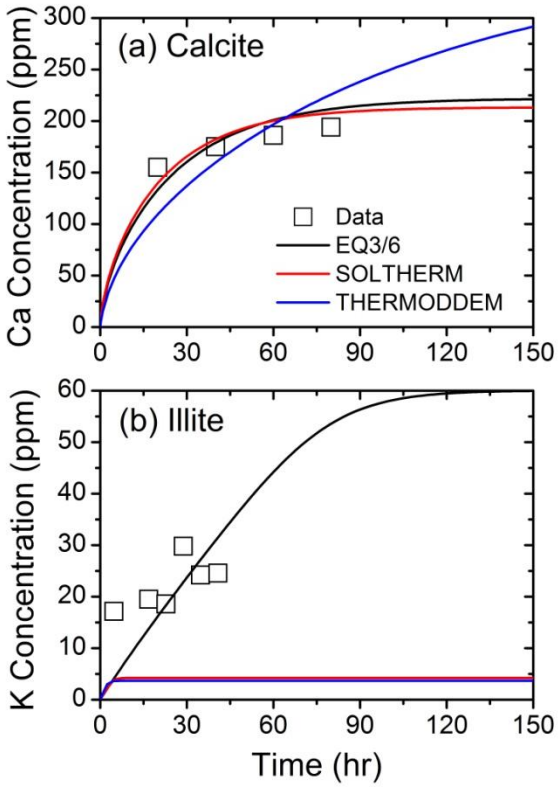


Figure 1: Changes in modeled (a) Ca and (b) K concentrations as a result of dissolution of calcite and illite, respectively, in CO_2 saturated water, using different thermodynamic databases.

Estimation of Reactive Surface Area

In order to calibrate the geochemical model, the reactive surface area is estimated using the mineral dissolution profiles in CO_2 saturated water (water/CO_2 mixture). The dissolution profiles of chlorite, illite, and labradorite are shown in Fig. 2, and the data for calcite and dolomite can be found in Petro et al. (2012). The model predictions with the calibrated reactive surface area are shown in solid lines.

For chlorite, the match between the measured and the simulated magnesium concentrations is good both at 120 °C and 150 °C, and the dissolved magnesium concentration increases linearly over the investigated

reaction time (see Fig. 2a). The mineral saturation index (log(Q/K)) at the last measurement time (58 hr for 120 °C and 40 hr for 150 °C) is -13.9 and -6.1 at 120 °C and 150 °C, respectively, indicating the fluid is undersaturated with respect to chlorite and still far from equilibrium (this is also indicated by the lack of a concentration plateau in the experimental data). Therefore, as discussed in the previous section for calcite dissolution, the estimated parameter should be accepted with caution, or a test with a longer reaction time should be considered to improve the validity of the calibrated model.

For illite dissolution, the residuals (the differences between the observations and the model predictions) are significantly large, particularly at 120 °C, which suggests that the model failed to account for the true system. The predicted dissolved potassium concentration at equilibrium based on log(K) values from the thermodynamic database is 31.2 ppm at 120 °C, whereas the highest concentration measured during the test period is 59.7 ppm. On the other hand, the match between the measurements and the modeled values is acceptable at 150 °C, even though it might be desirable to have more measurements for a longer reaction time to reduce the uncertainty in the calibrated model.

In the case of labradorite, the dissolution reaction appears to have reached equilibrium at 120 °C, and the calibrated model is also able to reproduce the measured values. At 150 °C, the modeled calcium concentrations are lower than the measured data, indicating the solubility data of labradorite in the thermodynamic database might not be accurate in all temperature and fluid composition ranges.

Table 1 summarizes the estimated reactive surface areas in comparison with the BET surface areas. The estimated reactive surface areas are smaller than the BET surface areas, and the difference ranges from a factor of about 2.5 for chlorite to up to five orders of magnitude for dolomite.

Table 1: Measured BET surface areas and estimated reactive surface areas. The values in parentheses are the marginal standard deviation of the estimated parameter.

Mineral	BET	Estimated	
		120 °C	150 °C
		[$cm^2\ g^{-1}$]	
Calcite	1.09×10^{3}	1.35×10^{-1} ($\pm\ 2.13\times10^{-2}$)	7.91×10^{-2} ($\pm\ 1.5\times10^{-2}$)
Dolomite	1.37×10^{3}	4.14×10^{-2} ($\pm\ 9.53\times10^{-3}$)	6.96×10^{-3} ($\pm\ 6.43\times10^{-4}$)
Chlorite	7.48×10^{2}	3.04×10^{2} ($\pm$ 39.7)	2.58×10^{2} ($\pm$ 78.0)
Labradorite	4.86×10^{3}	64.3 ($\pm$ 3.25)	24.9 ($\pm$ 0.70)
Illite	-	4.5×10^{5} ($\pm\ 3.66\times10^{5}$)	1.13×10^{5} ($\pm\ 1.82\times10^{4}$)

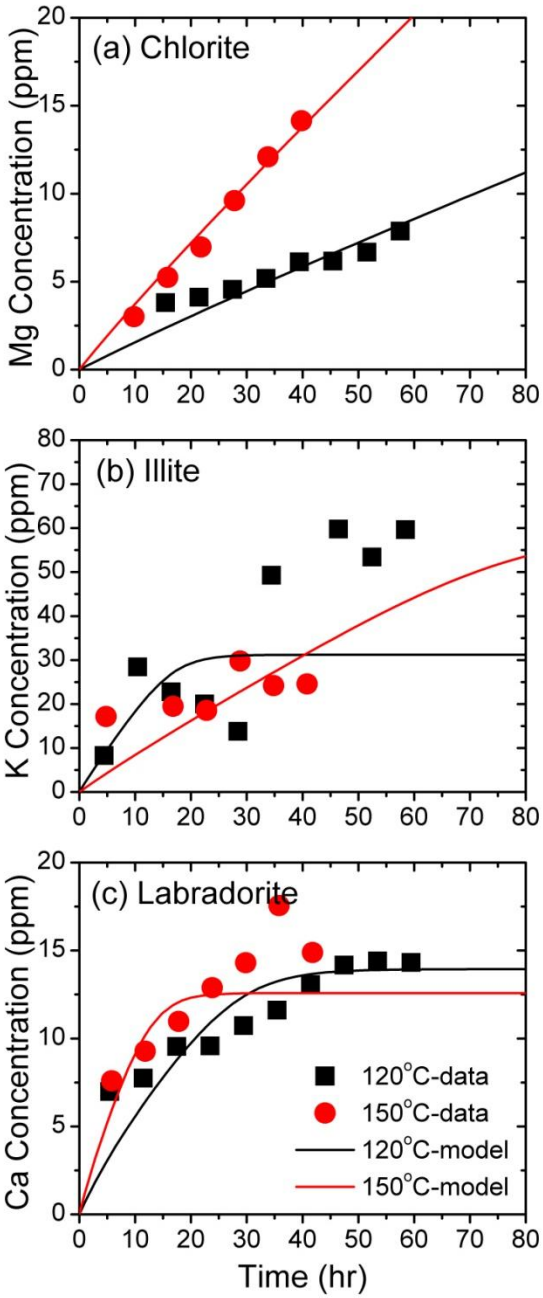


Figure 2: Measured and modeled (a) Mg, (b) K, and (c) Ca concentrations over time as a result of dissolution of chlorite, illite, and labradorite, respectively.

APPLICATION EXAMPLE: MODELING OF GEOCHEMICAL INTERACTION IN A CO_2-GEOTHERMAL SYSTEM

Using the thermodynamic and kinetic data calibrated from the CO_2-based experiments as mentioned in previous sections, we have performed reactive transport modeling to study the impact of fluid-rock interactions on a CPG system. Flow and geochemistry conditions are based on observations from the Cranfield site (e.g., Liu et al., 2012) for the modeling analyses.

Problem Setup

We employ a five-spot pattern as used in Pruess (2008) for modeling heat transfer and fluid dynamics of a CO_2-EGS (Fig. 3). The CO_2 geothermal reservoir is modeled as a porous medium system. The symmetry of the five-spot well pattern allows to limit the model to a 1/8 symmetry domain. The reservoir unit is based on Cretaceous Lower Tuscaloosa formation at the Cranfield CO_2 sequestration site, as reported by Liu et al. (2012). A reservoir thickness of 25 m is used. Fluid circulation is induced by specifying a pressure drop of 3 bar between the injection and production sides of the reservoir. We consider the injection of CO_2 into an initially water-saturated reservoir at temperature and pressure conditions of 150°C and 318.5 bar. The injection temperature is 20°C with a pressure of 320 bar, while fluid production occurs against a downhole pressure of 317 bar. The geometrical and hydrogeological parameters used are given in Table 2.

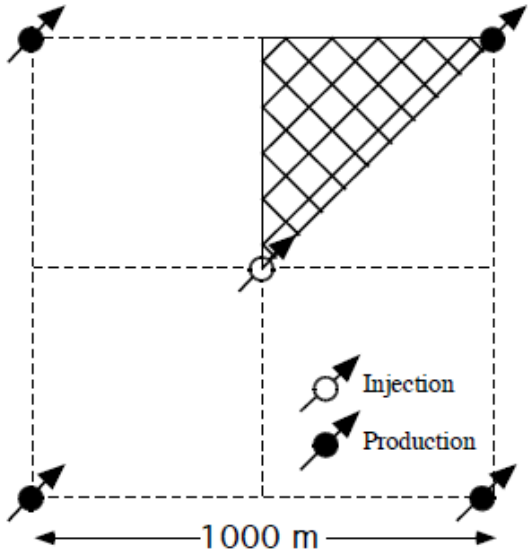


Figure 3: Five-spot well pattern with computational grid for modeling a 1/8 symmetry domain.

The initial mineralogical composition used in the model is taken from the average values given in Table 1 of Liu et al. (2012), and is summarized in Table 3. Siderite, ankerite, dawsonite, and smectite could be formed after CO_2 injection, and therefore are specified as secondary minerals in the simulation. Smectite is modeled using two end-members: Na-smectite and Ca-smectite. Reactive surface areas for the kinetics of mineral reactions used (Table 3) are taken from the calibration of the present CO_2-based experiments, as reported in the previous sections.

Table 2: Geometrical and hydrogeological specifications for the simulation.

Formation	
thickness	25 m
permeability	1.0×10^{-13} m^2
rock grain density	2650 kg/m^3
rock specific heat	920 J/kg/°C
rock thermal conductivity	2.51 W/m/°C
Initial Conditions	
reservoir fluid	all water
temperature	150 °C
pressure	318.5 bar
Production/Injection	
pattern area	1 km^2
injector-producer distance	707.1 m
injection temperature	20 °C
injection pressure (downhole)	320 bar
production pressure (downhole)	317 bar

Results and Discussion

Initial fluid production in response to supercritical CO_2 ($scCO_2$) injection is single-phase water (because the reservoir is initially water saturated). Breakthrough of $scCO_2$ at the production well occurs after about half a year, and subsequently a two phase water-CO_2 mixture is produced. Over time the gas (mainly $scCO_2$ and some vapor) saturations in the reservoir increase from the continuous $scCO_2$ injection. After about 3.5 yr, there is only gas phase in the produced fluid and this condition will last as long as CO_2 injection continues. At the time when an aqueous phase ceases to be produced, the produced CO_2 includes a few percent by weight of dissolved water. Water content (vapor) in produced gas will persist for a long time. The presence of dissolved water in the CO_2-rich phase may cause corrosive attack on reservoir rocks and well construction materials that require further investigation. Figure 4 shows the temperature distribution after 10 and 20 yr. Due to heat depletion in the reservoir, the temperature has gradually decreased. The peak of the thermal energy extracted occurs at 10 yr, and then the

production rate decreases: 7.6 MW at 5 yr, 8.8 MW at 10 yr, 8.3 MW at 15 yr, and 7.9 MW at 20 yr.

Table 3: Initial mineralogical compositions and reactive surface areas used in the model (the reactive surface area is an averaged one between calibrated values for experiments at 120 °C and 150 °C.

	Volume fraction (% of solid)	Reactive surface area (cm^2/g mineral)
Primary mineral:		
Quartz	0.794	9.8, from Xu et al. (2011)
Chlorite	0.118	4.464×10^{1}, Calibrated
Kaolinite	0.031	2.815×10^{5}, Set as illite
Illite	0.013	2.815×10^{5}, Calibrated
Calcite	0.011	1.071×10^{-1}, Calibrated
Dolomite	0.004	2.419×10^{-2}, Calibrated
Albite –Low	0.002	2.805×10^{2}, Set as labradorite
Non-reactive	0.027	
Secondary mineral:		
Siderite	0	2.419×10^{-2}, Set as dolomite
Ankerite	0	2.419×10^{-2}, Set as dolomite
Dawsonite	0	2.419×10^{-2}, Set as dolomite
Na-smectite	0	2.815×10^{5}, Set as illite
Ca-smectite	0	2.815×10^{5}, Set as illite

At the beginning of $scCO_2$ injection, CO_2 dissolution into groundwater lowers pH. The lowered pH induces dissolution of primary minerals and precipitation of secondary minerals. Significant chlorite dissolves especially close to the production side because of higher temperature there (Fig. 5). Small amounts of albite and quartz precipitation occurs. The carbonate mineral dolomite dissolves (Fig. 6). Some amount of calcite precipitation is obtained (Fig. 7). Tiny amounts of siderite, ankerite and dawsonite are formed. At the same time, the precipitation of clay minerals, smectite (Fig. 8) and illite, is observed. In general, more dissolution and precipitation occurs toward the production well along the main flow direction. The mineral reaction processes cause tiny decreases in porosity (Fig. 9). A small amount of CO_2 is sequestered by carbonate precipitation (Fig. 10), with a maximum value of 0.5 kg/m^3 medium. While Liu et al. (2012) observed no mineral dissolution and precipitation in their autoclave laboratory experiment of CO_2-water-rock interaction, it might be due to the much shorter reaction time (the total experimental time was 112 day, and CO_2 was introduced after 75 days).

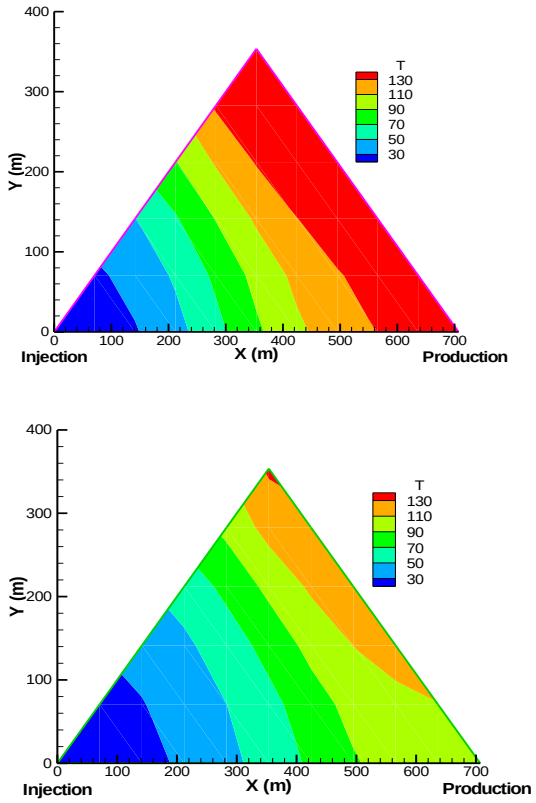


Figure 4: Simulated temperature distribution after 10 (top) and 20 (bottom) years.

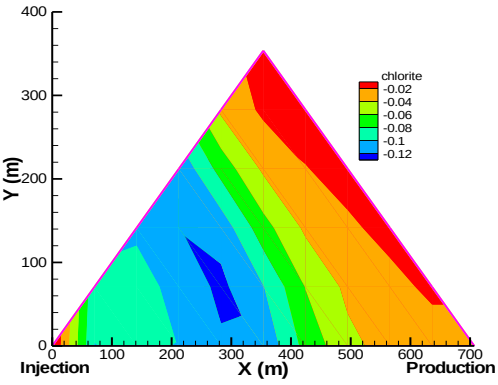


Figure 5: Changes of chlorite in volume fraction percent after 20 years (negative values indicate dissolution).

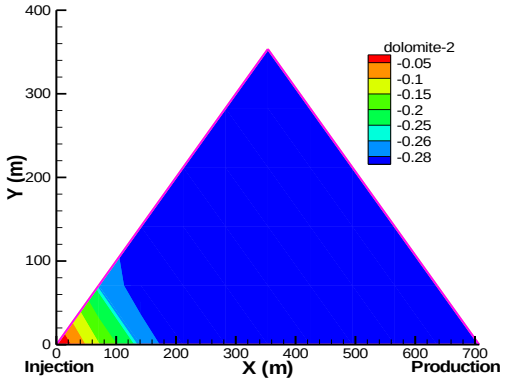


Figure 6: Changes of dolomite in volume fraction percent after 20 years.

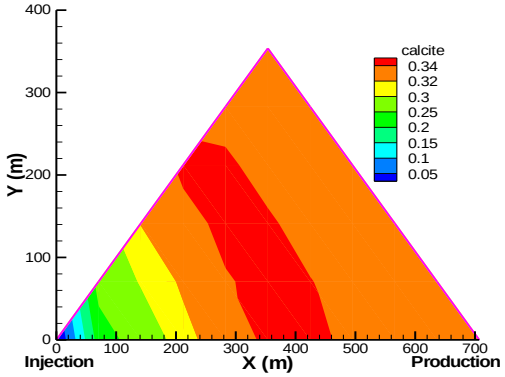


Figure 7: Changes of calcite in volume fraction percent after 20 years.

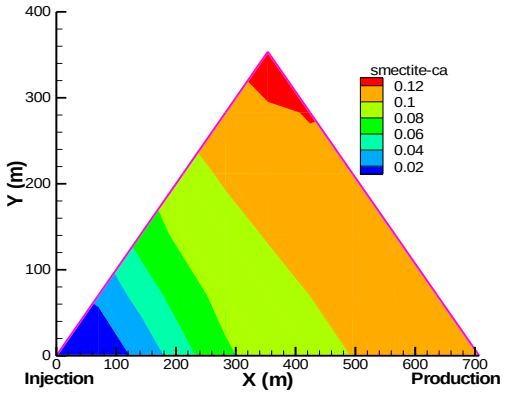


Figure 8: Changes of smectite in volume fraction percent after 20 years.

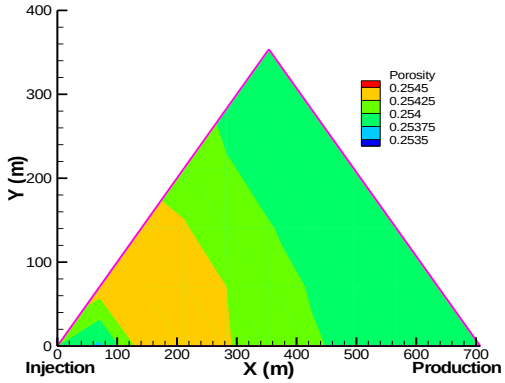


Figure 9: Porosity distribution after 20 years of operation (initial porosity is 0.254).

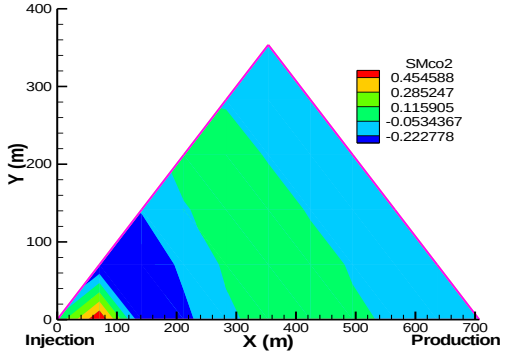


Figure 10: Total amounts of CO_2 sequestered by carbonate precipitation (kg/m^3 medium) after 20 years.

CONCLUSIONS

Based on the evolution of aqueous concentrations of selected cations in solutions derived from mineral dissolution experiments, we have performed TOUGHREACT batch geochemical modeling analyses and calibration. The dissolution kinetics and solubility of the minerals at the experimental conditions examined in this study are best described by the EQ3/6 database among the tested thermodynamic databases. The model calibration has also revealed that some of the experimental data, such as chlorite, have not leveled out to even quasi steady-state equilibrium conditions. For those cases, a longer experimental reaction period might be required to reduce the uncertainty in the calibrated kinetic parameters and to validate the applicability of the thermodynamic database.

Reactive transport modeling for a five-spot well configuration of a possible CO_2-geothermal system has been performed using thermal conditions and

mineralogical composition of the sandstone reservoir at the Cranfield CO_2 sequestration test site. Precipitation of carbonate and clay minerals doesn't significantly affect the porosity, and thus the flow circulation. Precipitation of carbonate minerals traps a small amount of CO_2 over the simulated injection period of 20 yr. It may be favorable for CO_2 storage for a long-term period of time after stopping CO_2 injection. Therefore, both sustained geothermal energy recovery and CO_2 geologic storage may be achieved.

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