

MINERAL CARBONATION IN A CO₂-EGS GEOTHERMAL RESERVOIR

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Abstract

There is growing interest in the novel concept of operating Enhanced Geothermal Systems (EGS) with CO₂ instead of water as heat transmission fluid. Initial studies have suggested that CO₂ may achieve larger rates of heat extraction, and can offer geologic storage of carbon as an ancillary benefit. Thermal and hydraulic aspects of a CO₂-EGS look promising. Major uncertainties remain with regard to chemical interactions. We have performed chemically reactive transport modeling to investigate fluid-rock interactions and CO₂ mineral carbonation of an EGS operated with CO₂. Two mineralogical compositions from EGS field sites and a wide range of temperatures were used in the present modeling analyses. The purpose is to identify subsurface environments that would be favorable for EGS with CO₂ especially for CO₂ mineral carbonation.

Key words: Mineral carbonation, Enhanced geothermal system, CO₂-EGS, Fluid-rock interaction, Geochemical modeling.

1. Introduction

With increasing concerns about carbon dioxide emissions into the atmosphere, Donald W. Brown (2000) proposed the new concept of operating Enhanced (or engineered) Geothermal Systems (EGS) with supercritical CO₂ instead of water as the heat transmission fluid. Such a scheme could combine recovery of geothermal energy with simultaneous geologic storage of CO₂. Compared with water, Brown noted that CO₂ has some favorable properties, including larger expansivity and lower viscosity, and is not a good solvent for rock minerals. He also pointed out unfavorable properties, such as lower specific heat of CO₂. In recent years, many studies have been undertaken to investigate various aspects relevant to CO₂-EGS systems, such as mechanical changes, CO₂-brine-rock reaction, heat transmission, and CO₂ mineralization or sequestration (Liu et al., 2003; Rosenbauer et al., 2005; Ueda et al., 2005; Pruess, and Azaroual 2006; Pruess 2006, 2008; Xu et al., 2008; Spycher and

Pruess, 2010; Wan et al., 2011). Advantages of EGS with CO₂ include increased heat extraction rates and wellbore flow compared to water-based systems, and lower potential for unfavorable rock-fluid chemical interactions (Pruess, 2006 and 2008). The solubility of CO₂ in water has implications for long-term carbon sequestration and water-rock interactions (Liu et al. 2003; Rosenbauer et al. 2005; Xu et al. 2006 and 2008).

The aqueous fluids initially present in the fractures of an EGS reservoir would be quickly removed by immiscible displacement by the CO₂, and by dissolution (evaporation) into the flowing CO₂ stream. Continuous operation of a CO₂-EGS may produce a rather dry CO₂ stream. Research on reactions between supercritical CO₂ and rocks in the absence of water has started only recently (Regnault et al., 2005; Jacquemet, 2006; McGrail et al., 2009). 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).

In the 2011 Stanford geothermal workshop, we (Wan et al., 2011) presented reactive transport simulations for a five-spot well configuration of a possible CO₂-EGS using thermal conditions and the mineralogical composition of Desert Peak Well DP 23-1 (Figure 1). Results indicate that a five-spot well pattern in a fractured reservoir is suitable for a CO₂-EGS operation. The fracture domain of the system is quickly filled with injected supercritical CO₂. Aqueous-phase based chemical reactions then stop, and no further mineral precipitation and porosity change occurs. On the other hand, the rock matrix remains in mixed two-phase CO₂-water conditions, and mineral alteration remains active for a long time. Precipitation of carbonate minerals can trap significant quantities of CO₂ in the matrix, favorable for CO₂ storage. Therefore, using this pattern we may achieve both sustained geothermal energy recovery and CO₂ geologic storage.

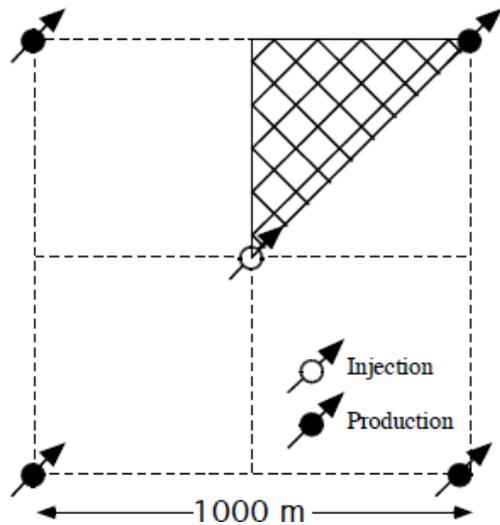


Figure 1. Five-Spot well pattern with computational grid for modeling a 1/8 symmetry domain.

Basic issues in CO₂-EGS systems include the physical and chemical changes induced by dissolved CO₂, including dissolution of primary minerals, formation of secondary minerals, CO₂ mineral trapping, and changes in reservoir porosity and permeability. In the present study, we examine water temperature and rock mineralogical conditions favorable for CO₂ mineral carbonation reactions.

2 PROBLEM SETUP

2.1 Geometric Representation of a Rock Matrix

We assume the fracture domain is quickly filled with injected supercritical CO₂. The reactions between dry supercritical (sc)CO₂ and rocks are not considered in the present work. The scCO₂ in the fractures surrounding the rock matrix penetrates the matrix by diffusion in both aqueous and gas (supercritical) phases. The MINC (multiple interacting continua) method was employed for modeling the fractured rock matrix (Figure 2). This method is designed to resolve “global” flow and diffusion of chemicals in the fractured rock and its interaction with “local” exchange between fracture and matrix rock. This method was first developed by Pruess and Narasimhan (1985) for fluid and heat flow in fractured porous media. The extension of the MINC method to reactive geochemical transport is described in detail by Xu and Pruess (2001). It is well-known that in the case of reactive chemistry diffusive fluxes may be controlled by reactions occurring near the fracture walls. The resolution of concentration gradients in matrix blocks is achieved by appropriate subgridding. The MINC concept is based on the

notion that changes in fluid pressures and chemical concentrations propagate rapidly through the fracture system, while invading the tight matrix blocks only slowly. Therefore, changes in matrix conditions will be (locally) controlled by the distance from the fractures and can then be modeled by means of one-dimensional strings of nested grid blocks.

Figure 2 shows an areal view of a rock matrix column that is surrounded by vertical fractures with a spacing of 0.5 m, with subgridding of the matrix using the MINC method. Subgrid 1 represents the fracture domain which is defined to include 50 percent by volume of wall rock. Subgrids 2 through 7 represent the rock matrix. Only one fracture-matrix domain is modeled, which could represent a portion of the central zone or “core” (Zone 1) in which all aqueous phase has been removed in fractures by dissolution into the flowing CO₂ stream (Figure 3).

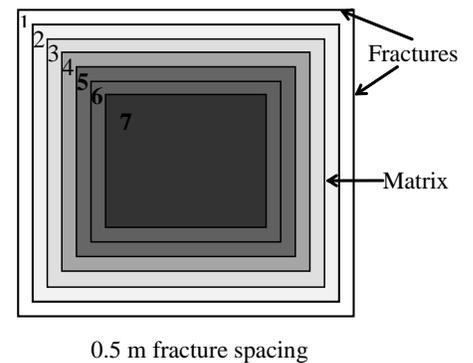


Figure 2. Subgridding of a rock matrix using the method of “multiple interacting continua” (MINC). The figure represents an areal view of a rock matrix column that is surrounded by vertical fractures.

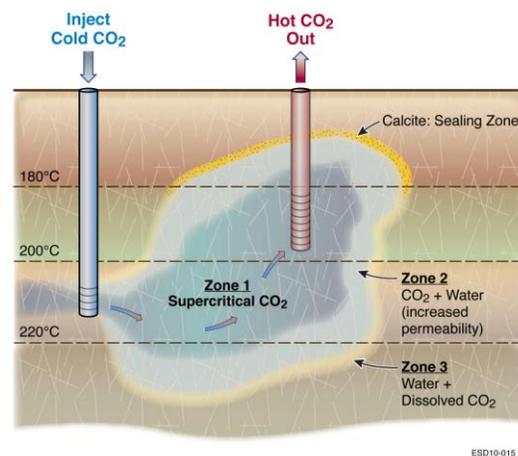


Figure 3. Schematic of the three zones created by injection of CO₂ into hot fractured rock (after Fouillac et al., 2004; Ueda et al., 2005).

2.2 Mineralogical Composition and Temperature

Two rock mineralogical compositions were used for the present modeling analyses, which are summarized in Table 1. The first composition was based on the mineralogy of the siliceous rhyolite tuff of DP Well 27-15 of the Desert Peak Enhanced Geothermal Field (Figure 4), reported by Lutz et al. (2010). A stimulation test was proposed in this well. Plagioclase was modeled using 50% low-albite and 50% anorthite. Other trace minerals including epidote, pyrite, and biotite were not considered in the model, because their reactions with the injected fluid are slow and less important chemically. The second is the unaltered granite from the Soultz European EGS site (Bächler, 2003).

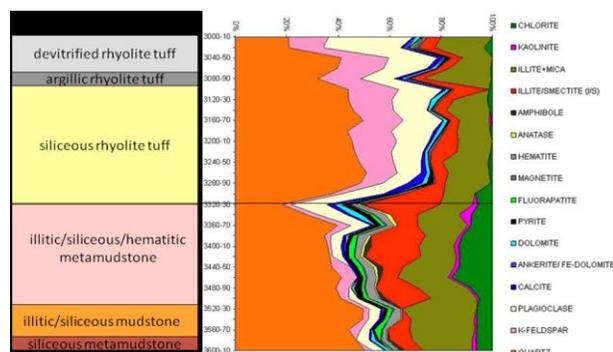


Figure 4. General lithotypes and whole-rock X-ray diffraction (XRD) mineralogy of well cutting samples in the planned stimulation interval of Well DP 27-15 (in relative weight percent). The figure was taken from Lutz et al. (2010).

Dolomite, siderite, ankerite, dawsonite, smectite, and kaolinite could be formed after CO₂ injection and are specified as secondary minerals in the model. Almost all possibilities of secondary carbonate and clay minerals could be covered in our simulations, which are based on previous modeling studies (Xu et al., 2008 and 2010). Parameters for the kinetics of mineral reaction used in the model, such as specific reactive surface area and kinetic parameter k_{25} and E_a , were taken from Xu et al. (2009 and 2010).

A wide range of temperatures (30, 60, 90, 120, 150, 165, 180, 195, 210 and 240°C) were used for the modeling analyses. A period of 10 years was simulated in the model.

Table 1. Initial mineralogical compositions used in the modeling analyses.

Mineral	Siliceous rhyolite tuff, DP Well 27-15	Unaltered granite, Soultz
Quartz	43	25.4
K-feldspar	15	23.6
Albite	7.5	21.25
Anorthite	7.5	21.25
Kaolinite	5	
Illite	18	
Biotite		4.2
Chlorite	1	4
Ankerite	1	
Calcite	1	0.3
Dolomite	1	

2.3 Simulation tool

The present simulations employed the nonisothermal reactive transport code TOUGHREACT (Xu et al., 2011). This code introduces reactive chemistry into the multiphase fluid and heat flow code TOUGH2 (Pruess, 2004). A new fluid property module, ECO2H, based on Spycher and Pruess (2010) was used. This module provides an accurate description of the thermophysical properties of mixtures of water and CO₂ under conditions typically encountered in CO₂-EGS systems of interest ($12^{\circ}\text{C} \leq T \leq 250^{\circ}\text{C}$; $1 \text{ bar} < P \leq 600 \text{ bar}$).

A broad range of subsurface thermal-physical-chemical processes can be modeled 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. (2011).

3. Results and discussion

Simulation results are given in Figs. 5-11. The supercritical CO₂ in the fracture invades into the rock matrix mainly by diffusion in both liquid and gas phases. The CO₂ dissolution into groundwater increases the total dissolved CO₂ concentration and lowers pH initially (Figure 5). The lowered pH induces dissolution of primary minerals such as K-feldspar, anorthite, and chlorite. Dissolution of anorthite and chlorite (Figure 6) will supply Ca, Mg and Fe for precipitation of dolomite and ankerite (Figure 7). At the same time clay minerals such as smectite and kaolinite precipitate. The precipitation of carbonate minerals (Dolomite, ankerite and dawsonite) sequesters CO₂ (so called mineral trapping).

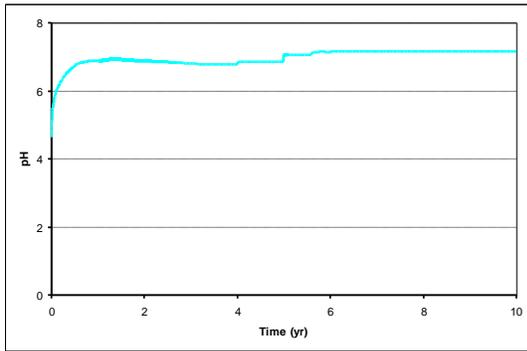


Figure 5. pH evolution over time for the first matrix grid block close to the fracture (Soultz unaltered granite, 165°C temperature).

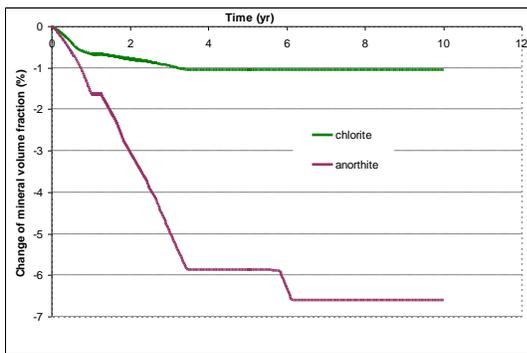


Figure 6. Dissolution (negative values of volume change) of anorthite and chlorite over time for the first matrix grid block close to the fracture (Soultz unaltered granite, 165°C temperature).

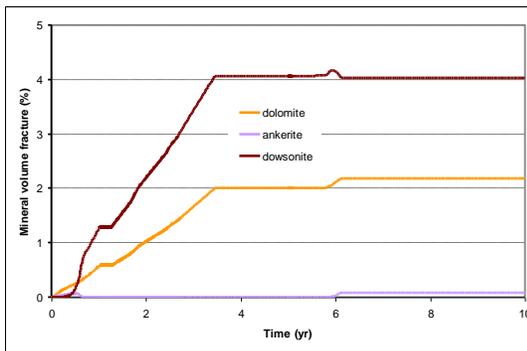


Figure 7. Precipitation (positive values of volume change) of anorthite and chlorite over time for the first matrix grid block close to the fracture (Soultz unaltered granite, 165°C temperature).

Quantities of CO₂ trapped in mineral phases after 10 years for the two types of rock at different temperatures (30, 60, 90, 120, 150, 165, 180, 195, 210, and 240°C) are presented in Figures 8 and 9, respectively. For both rock types, the curves of CO₂ trapped in carbonate minerals have peak values at 180-190 °C. Below 60°C, the CO₂ mineral trapping over 10 years is negligible, because kinetic rates of water-mineral reactions are slow at low temperatures. From 60°C to 185°C, the CO₂ mineral trapping gradually increases with increasing temperature. From 185°C to 210°C, the CO₂ mineral trapping decreases dramatically with increasing temperature. Above 210°C, the CO₂ mineral trapping is also very small, because at high temperatures water itself becomes acid (pH is around 5.5, water has a large dissociation constant at these temperatures, or logK is less than 14).

For Desert Peak siliceous rhyolite tuff, the peak value of mineral trapping is smaller than Soultz unaltered granite (16 compared to 83 kg/m³), but the former curve is elevated over a wider temperature range than the latter. This is because the two rock types have different mineral compositions. The volume fraction of chlorite (supplying Mg and Fe for carbonate precipitation) in siliceous rhyolite tuff is lower than that in Soultz granite (1 compared to 4%), and anorthite (Ca) has the same trend (7.5 compared to 21.25%).

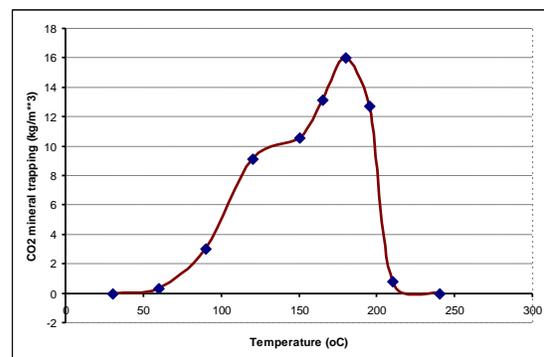


Figure 8. CO₂ mineral trapping (kg CO₂ per m³ medium) from 30°C to 240°C obtained with siliceous rhyolite Desert Peak DP Well 27-15 tuff after 10 years. Symbols are calculated values at the indicated temperatures.

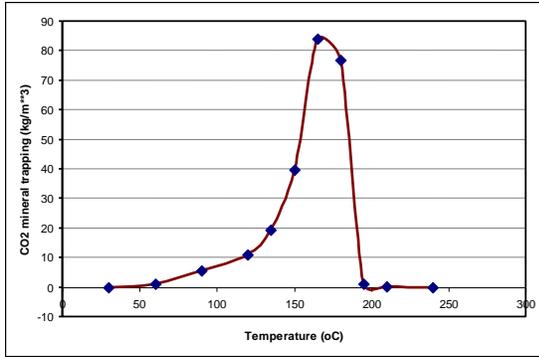


Figure 9. CO₂ mineral trapping from 30 °C to 240 °C obtained with Soutz unaltered granite (after 10 years).

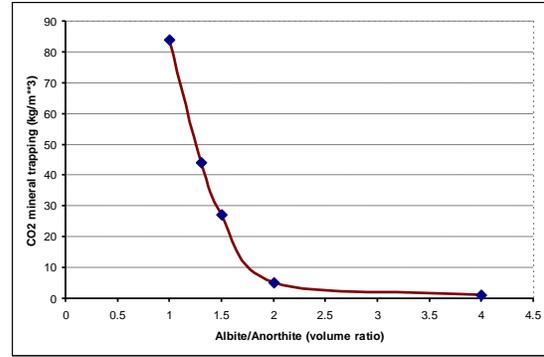


Figure 11. CO₂ mineral trapping for abundances of volume ratio of albite over anorthite based on Soutz unaltered granite (after 10 years).

Based on Soutz unaltered granite, we performed simulations using different amounts of chlorite (adjusted by changing the quartz volume fraction). CO₂ mineral trapping increases almost linearly with chlorite volume fraction (Figure 10). We also carried out simulations using different volume ratios of albite (Na feldspar) and anorthite (Ca feldspar). The trapping decreases with increasing albite/anorthite ratio (Figure 11), or the higher the Ca content in the plagioclase, the larger the CO₂ mineral trapping.

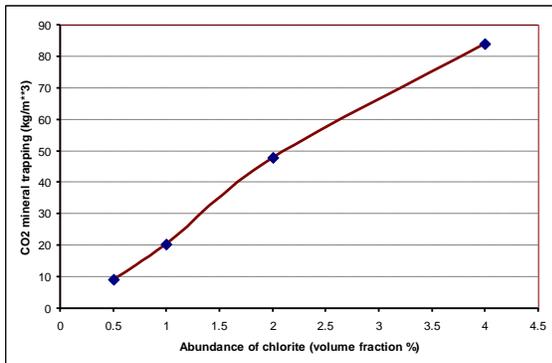


Figure 10. CO₂ mineral trapping for chlorite volume fraction (%) based on Soutz unaltered granite (after 10 years).

4. Conclusions

Geochemical modeling of two types of rock for fractured CO₂-EGS reservoirs using a range of temperatures has been performed. We assume that the fracture domain of the system is quickly filled with injected supercritical CO₂. The rock matrix remains under mixed two-phase CO₂-water conditions, and mineral alteration remains active for a long time. Precipitation of carbonate minerals traps significant quantities of CO₂ in the matrix, favorable for CO₂ storage.

Modeling results indicate that a rock with higher contents of Ca, Mg, and Fe (such as anorthite and chlorite), is more favorable for CO₂ mineral carbonation in CO₂-EGS reservoirs. The most favorable temperatures for the mineral trapping are between 160 °C and 190 °C. Other mineral compositions and temperature ranges are less favorable for carbonate precipitation.

This paper presents a method to identify subsurface environments favorable for EGS with CO₂ operation and for CO₂ mineral carbonation. The long-term geochemical behavior could be crucial for sustaining energy recovery, for estimating CO₂ loss rates, and for figuring tradeoffs between geothermal power generation and geologic storage of CO₂.

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