

NUMERICAL SIMULATIONS OF INTERACTIONS BETWEEN SUPERCRITICAL CO₂ AND HIGH-TEMPERATURE FRACTURED ROCKS IN ENHANCED GEOTHERMAL SYSTEMS

Feng Pan^{1,2}, Brian J O L McPherson^{1,2}, Peter C Lichtner³, Satish Karra³,
Caroline Lo Ré⁴, John P Kaszuba⁴, Chuan Lu⁵, Tianfu Xu⁶

¹Energy & Geosciences Institute, The University of Utah, Salt Lake City, UT, United States.

²Department of Civil and Environmental Engineering, The University of Utah, Salt Lake City, UT, United States.

³EES-16, Los Alamos National Laboratory, Los Alamos, NM, United States.

⁴Geology & Geophysics, The University of Wyoming, Laramie, WY, United States.

⁵Idaho National Laboratory, Idaho Falls, ID, United States.

⁶Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States.

423 Wakara Way, Suite 300
Salt Lake City, UT 84108, U.S.A
e-mail: fpan@egi.utah.edu

ABSTRACT

Supercritical CO₂ has been suggested as a heat transmission fluid in Enhanced Geothermal Systems (EGS), to improve energy extraction. Additionally, most engineered CO₂-flow systems, such as enhanced oil recovery reservoirs, lose a significant percentage of injected CO₂ by virtue of simple migration out of the system. Thus, EGS reservoirs utilizing CO₂ as a working fluid will most likely foster carbon sequestration as a collateral result. The chemical interactions between supercritical CO₂ and fractured rocks at high temperature and pressure in EGS reservoirs have yet to be comprehensively investigated. The data for kinetic rate constants of mineral reactions are sparse and less consistent. Mineral surface and its evolution with time are difficult to quantify. The objectives of this work are: (1) to calibrate and evaluate kinetic rate constants of minerals based on the batch experimental data collected by researchers at the University of Wyoming (UW) (Lo Ré et al., this volume); (2) to evaluate the possible effects of supercritical CO₂ interactions with EGS reservoir rocks at various conditions of pressures, temperatures, and salinities. Batch experiments are underway at UW to investigate the geochemical reactions among water, fractured granite rocks, and injected supercritical CO₂. The batch simulations are firstly conducted to mimic the laboratory experiments for the calibration of kinetic rates using TOUGHREACT and PFLOTRAN models. We developed a series of 2-D numerical simulations of CO₂ as an EGS working fluid at various conditions of pressures, temperatures, and salinities using the well-known TOUGH2

geothermal simulator (Pruess et al., 1999). Results of our numerical studies suggest that employing supercritical CO₂ as a working fluid in EGS reservoirs may enhance injectivity, mass flow rate, and heat extraction efficiency, at least compared to hydrothermal brine. Our simulations also suggest that EGS design may be optimized to enhance geothermal energy extraction and facilitate concomitant CO₂ sequestration.

INTRODUCTION

Supercritical CO₂ (scCO₂) has been suggested as a heat transmission fluid in Enhanced Geothermal Systems (EGS) to improve energy extraction and CO₂ sequestration (Brown, 2000; Pruess, 2007, 2008). Advantages of CO₂ as a heat transmission fluid include its larger expansivity, lower viscosity, and that it is a poor solvent for rock minerals compared to water (Brown, 2000). Disadvantages of CO₂ as a working fluid include its lower mass heat capacity than water (Brown, 2000; Pruess, 2007). Understanding the properties of supercritical CO₂ and CO₂-brine-rock interactions at high temperatures is particularly important to quantify the relative ability of CO₂ to enhance energy extraction and sequestration in EGS reservoirs.

Much research related to CO₂-EGS systems has been conducted recently, including experiments and numerical simulations of heat extraction, CO₂-brine-rock interactions, geochemical processes of fluid-rock reaction, and CO₂ mineralization or sequestration etc. (André et al., 2007; Newell et al., 2008; Pruess, 2007, 2008; Rosenbauer et al., 2005; Wan et al., 2011; Wigand et al., 2009; Xu et al.,

2004, 2008). Pruess (2007, 2008) compared CO₂ and water with respect to heat extraction rate and mass flow rate in EGS reservoirs. Heat extraction and flow rate largely increase with CO₂ as the working fluid instead of water, indicating good potential for CO₂ use in EGS reservoirs. Rosenbauer et al. (2005) experimentally tested CO₂-brine-rock interactions at 120 °C and 200-300 bar. Results suggested that solubility of CO₂ may enhance water-rock interaction and CO₂ sequestration in carbonate mineral phases. Wan et al. (2011) and Xu et al. (2008) simulated geochemical processes of fluid-rock interaction with CO₂ as the working fluid under high pressure and temperature, and showed that significant CO₂ may be stored in EGS reservoirs by mineral trapping due to precipitation of carbonate minerals. Xu et al. (2004) also performed batch geochemical simulations for three different aquifer mineral compositions, to evaluate long term CO₂ disposal in deep aquifers. Results suggested that CO₂ sequestration by mineral trapping varies largely with rock type and mineral composition, and porosity is reduced due to precipitation of carbonates. André et al. (2007) conducted numerical modeling of fluid-rock chemical interactions of two CO₂ injection scenarios, CO₂-saturated water and supercritical CO₂, in a deep carbonate aquifer. Their results illustrated that geochemical activity with supercritical CO₂ injection was much lower than simulations of CO₂-saturated water injection.

Although previous studies have been conducted for CO₂ as a working fluid in EGS reservoirs, the chemical interactions of supercritical CO₂ and fractured rocks at high temperature and pressure in EGS reservoirs have yet to be comprehensively investigated. The data for kinetic rate constants of mineral reactions are sparse and less consistent at these conditions. In addition, the energy extraction at various conditions of pressures, temperatures, and salinities for CO₂ as working fluid in EGS reservoirs has not been fully examined. The objectives of this work are: (1) to calibrate and evaluate kinetic rate constants and reactive surface area of minerals based on the batch experimental data collected by collaborators at University of Wyoming; (2) to evaluate the possible effects of supercritical CO₂ interactions with EGS reservoir rocks at various conditions of pressures, temperatures, and salinities.

METHODS AND MATERIALS

Batch experiment and simulation

Collaborators at UW are conducting equilibrium modeling and hydrothermal experiments to evaluate the effects of scCO₂ injection on a granitic reservoir (Lo Ré et al., this volume). Experiments are being

conducted in rocking autoclaves using flexible Au-Ti reaction cells. Reactants include a synthetic groundwater, a two-feldspar/quartz/biotite granite, and scCO₂. Three experiments have been completed including a baseline water-granite experiment and two water-granite-scCO₂ experiments. Modeling and experiments were conducted at 250 °C and 250-450 bar. Each experiment started as a water-granite experiment that was allowed to react for ~28 days. For two of the experiments, the systems were then injected with scCO₂ and allowed to react for at least an additional 42 days. Batch experiment details are included in Lo Ré et al. (2012).

The batch simulations are conducted to mimic the laboratory experiments for the calibration of kinetic rates using non-isothermal reactive transport code TOUGHREACT (Xu et al., 2004), and multiscale-multiphase-multicomponent subsurface reactive flow model PFLOTRAN (Hammond et al., 2010). Current batch simulations use the aqueous data from one of the batch experiments described above. Analysis of mineral dissolution and precipitation results is currently underway at the UW. When complete, results will be incorporated into subsequent batch simulations.

Problem setup for supercritical CO₂ as a working fluid

A 2-D domain shown in Figure 1 was designed to evaluate mass flow and heat extraction rates associated with use of scCO₂ as the EGS working fluid. The model domain of EGS reservoir is 1100m × 500m horizontally, with a thickness of 100m; the total number of model grid nodes is 11×5×1 = 55. We also employed a dual-continuum approach to simulate the fracture-matrix heat flow transfer, with fracture spacing of 50m and fracture volume fraction of 2%. The distance of injection and production wells was 1000m with a certain pressure drop of 25 bar. The Dirichlet condition with constant pressure was set as the boundaries of injection and production sides and the Neumann condition (no flow) was assigned on all other sides. Initial conditions included temperature of 200 °C and pressure of 200 bar in the EGS reservoir. Details of hydrological properties, initial condition, and injection/production conditions are listed in Table 1.

Numerical models

A fluid property module of TOUGH2 code, ECO2H, was employed to simulate the mass flow and heat extraction rates for supercritical CO₂ as working fluid in EGS reservoir. The reactive transport models, TOUGHREACT and PFLOTRAN were used to mimic the laboratory experiments for calibration and evaluation of kinetic rates.

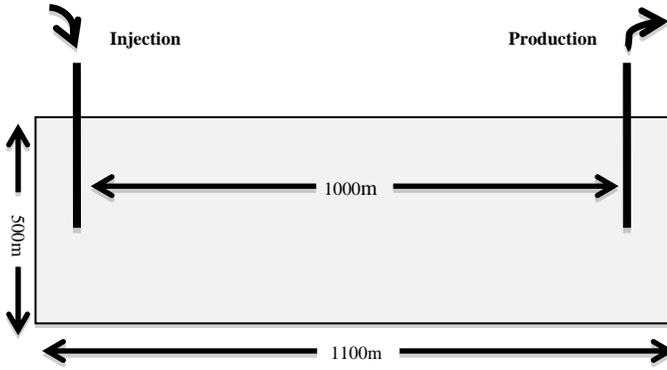


Figure 1: Geometry of 2-D model domain.

Table 1: Hydrologic parameters, initial, and production/injection conditions.

Properties	
Fractured rock permeability	10^{-13} m^2
High Granite permeability:	10^{-17} m^2
Fracture spacing	50 m
Fracture volume fraction	2%
Fracture Porosity:	0.50
Fracture Tortuosity:	1.0
Thermal conductivity:	$2.51 \text{ W/m } ^\circ\text{C}$
Rock specific heat:	$1000 \text{ J/kg } ^\circ\text{C}$
Rock grain density	2650 kg/ m^3
Initial Condition	
Reservoir fluid	water only
Initial temperature:	200°C
Initial pressure	200 bar
Production/Injection condition	
Injection/production distance	well 1000 m
Injection pressure	200 bar
Injection temperature	50°C
Production pressure	175 bar

The ECO2H equation-of-state (EOS) algorithm was designed for applications to geologic sequestration of CO_2 in saline aquifers at high temperature and pressure (Pruess, 2005; Pruess and Spycher, 2010). This EOS can provide an accurate and comprehensive description of thermodynamics and thermophysical properties of water-brine- CO_2 mixtures under the conditions of temperature up to 300°C and pressure up to 600 bar (Wan et al., 2011).

TOUGHREACT was developed to simulate non-isothermal multi-component reactive fluid flow and geochemical transport by introducing reactive geochemistry into the existing multiphase flow and heat flow code TOUGH2 (Xu et al., 2006). TOUGHREACT has been applied to subsurface thermo-physical-chemical processes in various environmental problems and geologic systems.

PFLOTRAN is a massively parallel, multiphase-multicomponent, reactive flow and transport code that runs on peta-scale high performance computing architectures to laptops (Hammond et al., 2010). It is based on PETSc for its parallel framework using domain decomposition. It has been applied to CO_2 sequestration and geothermal energy recovery and contaminant migration in field-scale sized problems (Hammond and Lichtner, 2010).

RESULTS

Batch simulation

Simulations of the UW batch experiments were conducted using PFLOTRAN and TOUGHREACT, but without flow, to mimic the batch conditions. PFLOTRAN and TOUGHREACT were run with a single grid cell to represent the reactor vessel. Input to PFLOTRAN and TOUGHREACT requires specifying the initial volume fractions and surface areas of the primary mineral assemblage together with the initial fluid composition. The thermodynamic database used for the batch simulations was taken from EQ3/6 database.

The primary simulation minerals, equivalent to those used in the batch experiments, were quartz, oligoclase, albite, K-feldspar, annite, and phlogopite. Table 2 lists the chemical compositions and initial volume fractions of primary minerals and possible secondary minerals. Kinetic properties (rate constant, activation energy, and power term) of multiple mechanisms (neutral, acid and base) for primary and secondary minerals are listed in Table 3. The specific reactive surface areas (S_m) of primary minerals are calculated as (Perez ad Boles, 2005):

$$S_m = \frac{6}{d} \nu \quad (1)$$

where: d is the grain diameter (cm); ν is the initial mineral volume fraction.

Simulation periods were 2000 hours. Simulated supercritical CO_2 was injected at 674.4 hours for 1 hour at a rate of $5.7611 \times 10^{-6} \text{ kg/s}$ with an equal and opposite rate of extraction of brine. Preliminary results using TOUGHREACT and PFLOTRAN are plotted in Figures 2 and 3, respectively. One can see from Figure 2 that the pH values gently increased from 3.85 to 5.25 before CO_2 injection, and sharply decreased from 5.25 to 3.79 with CO_2 injection at 674.4 hours. After 1-hour CO_2 injection, the pH values slowly increased to 5.05 at the end of batch simulation. The values of reaction rate of primary mineral quartz were negative before CO_2 injection

and become positive after CO₂ injection, indicating that the dissolution and precipitation of quartz before and after CO₂ injection, respectively. Opposite characteristics compared to quartz were observed for mineral albite, which precipitated before CO₂ injection and dissolved after CO₂ injection. It was also observed (Figure 2) that the reactive rates for other minerals are relatively smaller than quartz and albite. Comparisons of those results using TOUGHREACT in Figure 2 and PFLOTTRAN in Figure 3 show minor differences between them.

Table 2: Chemical composition and initial volume fraction for mineral used for batch simulation.

Mineral	Chemical composition	Volume fraction
		(%)
Primary:		
Quartz	SiO ₂	0.595
Oligoclase-uwyy ^a	Na _{0.77} Ca _{0.23} Al _{1.23} Si _{2.77} O ₈	0.464
Albite	NaAlSi ₃ O ₈	0.023
K-Feldspar	KAlSi ₃ O ₈	0.023
Annite	KFe ₃ AlSi ₃ O ₁₀ (OH) ₂	0.048
Phlogopite	KAlMg ₃ Si ₃ O ₁₀ (OH) ₂	0.039
Porosity	-	98.759
Total		99.951
Secondary:		
Calcite	CaCO ₃	0.0
Magnesite	MgCO ₃	0.0
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	0.0
Diaspore	AlHO ₂	0.0
Siderite	FeCO ₃	0.0
Gibbsite	Al(OH) ₃	0.0
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	0.0
Paragonite	NaAl ₃ Si ₃ O ₁₀ (OH) ₂	0.0
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	0.0
Chalcedony	SiO ₂	0.0
SiO ₂ (am)	SiO ₂	0.0
Boehmite	AlO(OH)	0.0
Analcime	NaAlSi ₂ O ₆ H ₂ O	0.0

a) Oligoclase at specific ratio used for batch experiment by The University of Wyoming.

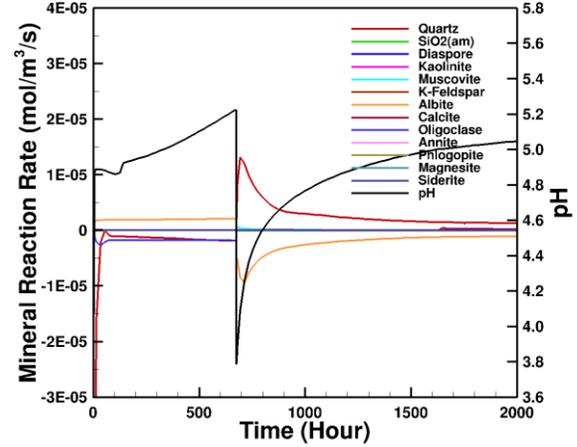


Figure 2: Simulated pH and mineral reaction rates using TOUGHREACT model.

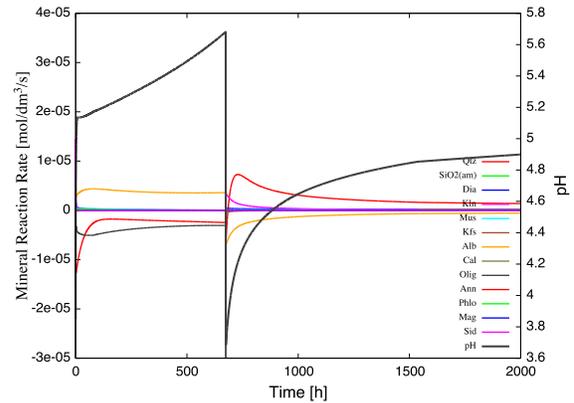


Figure 3: Simulated pH and mineral reaction rates using PFLOTTRAN model.

Simulation with supercritical CO₂ as a working fluid

Figure 4 shows simulated mass flow rate, net heat extraction, temperature, and gas saturation for CO₂ as a working fluid. Similar results for water as the working fluid are also plotted in Figure 4. The flow containing water only is produced with the rate of 40 kg/s at the initial stage of simulation. After 0.1 year, the water flow rate sharply decreases with the increase of CO₂ flow rate, demonstrating the mixture of water and CO₂ is produced when the CO₂ flow has reached the production well. With continuous CO₂ injection and increase of gas saturation close to the production well, CO₂ flow rate significantly increases with no more water flow production. The oscillations of CO₂ and water flow rate are due to water dry-out in the fractures of partial reservoir. The net heat extraction is around 28 MW in the initial stage of simulation and decreases to 10 MW after 0.1 years, which has similar trend to water flow rate. With increases of CO₂ flow rate, the next heat extraction increase to 24 MW after 4 years of CO₂ injection.

Table 3: Kinetic rate parameters for minerals used for the batch simulation.

Mineral	Neutral Mechanism		Acid Mechanism			Base mechanism		
	logk ^a	E _a ^b	logk ^a	E _a ^b	n ^c	logk ^a	E _a ^b	n ^c
Primary:								
Quartz	-13.99	87.7	-	-	-	-	-	-
Oligoclase	-11.84	69.8	-9.67	65.0	0.457	-	-	-
Albite	-12.56	69.8	-10.16	65.0	0.457	-15.6	71.0	-0.572
K-Feldspar	-12.41	38.0	-10.06	51.7	0.500	-21.2	94.1	-0.823
Annite ^d	-12.55	22.0	-9.84	22.0	0.525	-	-	-
Phlogopite	-12.40	29.0	-	-	-	-	-	-
Secondary:								
Calcite	-5.81	23.5	-0.30	14.4	1.000	-	-	-
Magnesite	-9.34	23.5	-6.38	14.4	1.000	-	-	-
Kaolinite	-13.16	22.2	-11.31	65.9	0.777	-17.05	17.9	-0.472
Diaspore	-13.33	47.5	-	-	-	-23.60	47.5	-1.503
Siderite	-8.90	62.8	-3.19	36.1	0.500	-	-	-
Gibbsite	-11.50	61.2	-7.65	47.5	0.992	-16.65	80.1	-0.784
Muscovite	-13.55	22.0	-11.85	22.0	0.370	-14.55	22.0	-0.220
Paragonite	-13.00	22.0	-	-	-	-	-	-
Pyrophyllite	-12.40	29.0	-	-	-	-	-	-
Chalcedony ^e	-13.99	87.7	-	-	-	-	-	-
SiO ₂ (am)	-12.23	74.5	-	-	-	-	-	-
Boehmite ^f	-13.33	47.5	-	-	-	-23.60	47.5	-1.503
Analcime ^g	-8.56	65.4	-2.73	62.9	1.130	-10.76	37.8	-0.200

Note: Kinetic rate parameters from Palandri and Kharaka (2004);

a) logk: kinetic rate constant k at 25 °C (mol/m²/s); b) E_a: activation energy (KJ/mol);

c) n: power term with respect to H⁺; d) set to Biotite; e) set to Quartz;

f) set to Diaspore; g) set to Nepheline.

After 4 years with fully saturated CO₂ at production well, the net extraction decreases to 10 MW after 50 years of CO₂ injection. This is due to more rapid thermal depletion of CO₂ compared to water. This can be observed from rapid decrease of simulated temperature after CO₂ is fully saturated close to the production well (Figure 4b). The temperature next to the injection well gently decreases from the initial temperature of 200 °C to the injection temperature of 50 °C. The CO₂ saturation next to the injection well becomes fully saturated after 0.4 years of CO₂ injection.

The mass flow rates next to injection and production wells almost keep constant at 20 kg/s for water as working fluid, which are much smaller than 40 kg/s of water flow rate at the initial stage and 40-70 kg/s of CO₂ flow rate after full CO₂ saturation reached in the CO₂ working fluid simulation. We attribute this to lower viscosity of CO₂ compared to water. The net heat extraction for water as working fluid is almost constant at 12 MW before 10 years and decreases to 8 MW at 50 years of water injection. Compared to the results for CO₂ as working fluid, the net extraction rate for water as a working fluid is much

smaller at the initial stage of simulation and after 1 year of injection for water, indicating supercritical CO₂ as working fluid in EGS reservoirs could enhance heat extraction instead of water as working fluid. However, their differences of net heat extraction decrease with time after 4 years at fully saturated CO₂ reached. This is explained by more rapid thermal depletion using CO₂ than water, which is also verified by the relatively larger drop of temperature for CO₂ as working fluid compared to water (Figure 4b). It can also be seen from Figure 4a, the net heat extraction rate for CO₂ as working fluid is slightly smaller than the one for water as working fluid between 0.1 and 1 years of injection. This is because the relatively lower CO₂-water mixture production flow rate when CO₂ has reach production well and keeps low gas saturation.

Effects of injection/production pressure drop and initial salinity on heat extraction

Figure 5 plots simulated net heat extraction rate, mass flow rate, temperature, and gas saturation for CO₂ as working fluid at the injection/ production pressure drop of 10, 25, 50, and 100 bar, respectively. The

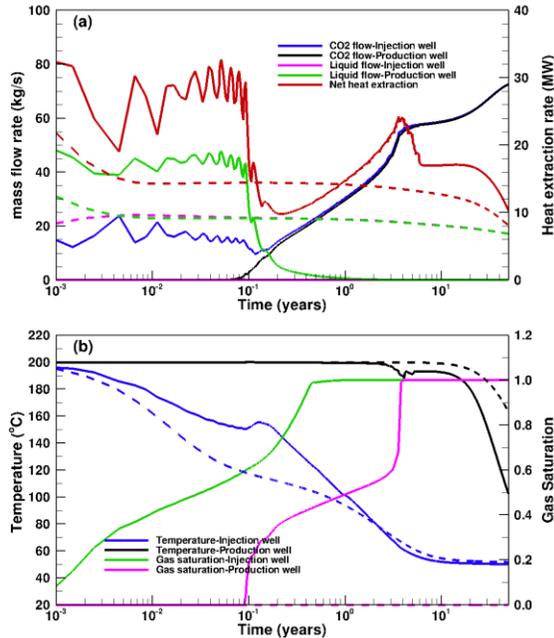


Figure 4: Simulated net heat extraction, mass flow rate, temperature, and gas saturation for both CO₂ (solid line) and water (dash line) as working fluids.

mass flow rates of water and CO₂ production show similar characteristics for different pressure drops, but their values are significantly different. For example, the water flow production rate in the initial stage of simulation are around 230, 100, 40, and 20 kg/s for pressure drop of 100, 50, 25, and 10 bar, respectively. The CO₂ flow rates close to the production well also significantly increased with pressure drop from 10, 25, 50 to 100 bar after fully saturated CO₂ is reached. This is driven by the large pressure gradient leading to larger mass flow rate. The net heat extraction rates for different pressure drops also show similar trends. However, after fully saturated CO₂ is reached, the gradient of net heat extraction rates with higher pressure drop is much larger than the one with smaller pressure drop, which is also similar to the temperature profiles (Figure 5b). This can be explained by the large pressure gradient that could lead to large mass flow rate and rapid temperature drop. Thus, the relatively smaller temperature differences of CO₂ between injection and production wells generate smaller density difference and less buoyancy force that could reduce the power consumption at production well (Pruess, 2007). After 50 years of CO₂ injection, the net heat extraction is 10 MW for the pressure drop of 25 bar and 5-7 MW for the pressure drops of 10, 50, and 100 bar, indicating the pressure drop of 25 bar is suitable for heat extraction in EGS reservoirs. It can be seen from Figure 5b that the fully saturated CO₂ next to production well is reached much faster with large

pressure drop than the one with small pressure drop. This is also explained by the large CO₂ flow rate driven by large pressure gradient.

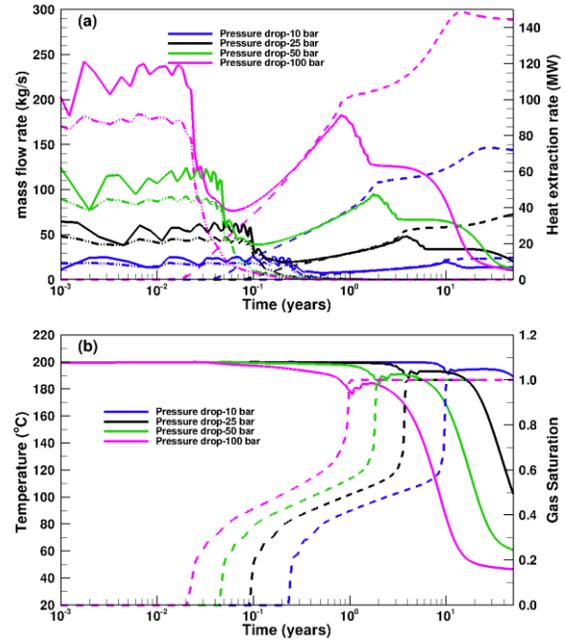


Figure 5: Simulated net heat extraction (solid line in 5a), mass flow rate (dash dot line in 5a for water flow; dash line in 5a for CO₂ flow), temperature (solid line in 5b), and gas saturation (dash line in 5b) with injection/production pressure drops at 10, 25, 50, and 100 bar for CO₂ as a working fluid.

Figure 6 depicts simulated net heat extraction rate, mass flow rate, temperature, and gas saturation for CO₂ as working fluid under different initial salinity. At the early stage of simulation, water production rate is around 40, 35, 27, and 25 kg/s for initial brine at 0%, 10%, 30%, and 50%, respectively. Correspondingly, the next heat extraction also decreases from 30 MW under 0% brine to 12 MW under 50% brine. The differences among CO₂ flow production rates under different initial salinity become smaller with continuous injection of CO₂. They are almost the same after 4 years of CO₂ injection. The next heat extraction also shows similar trend as the CO₂ mass flow rate. It indicates that the initial salinity has significant effects on heat extraction at the early stage of simulation. It is observed from Figure 6b that the temperature profiles are almost the same with different initial salinity. The gas saturation next to production well increases from 0.78 to 1.0 for initial brine from 50%, 30%, 10% to 0% after 50 years of CO₂ injection. It

demonstrates that the brine cannot be fully extracted from production well.

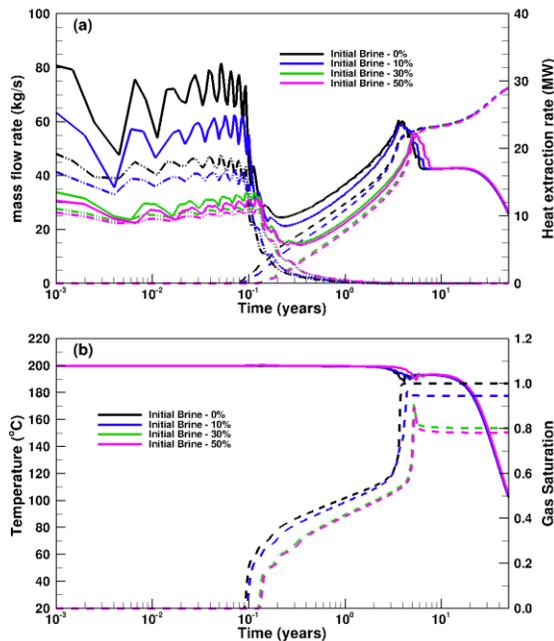


Figure 6: Simulated net heat extraction (solid line in 6a), mass flow rate (dash dot line in 6a for water flow; dash line in 6a for CO₂ flow), temperature (solid line in 6b), and gas saturation (dash line in 6b) with initial brine of 0%, 10%, 30%, and 50%.

CONCLUSIONS

The general purpose of this study was to improve and extend simulation methods for EGS reservoir analysis. Specifically, we conducted batch simulations to mimic laboratory experiments of water-CO₂-granite interactions for sake of calibration of kinetic rates of mineral reactions. The pH values of batch simulation gently increased in the early stages of these batch simulations, and sharply decreased with CO₂ injection. After 1 hour of simulated CO₂ injection, the pH values slowly increased until the end of simulation. Dissolution and precipitation of quartz occurred before and after CO₂ injection, respectively. Albite precipitates before CO₂ injection and dissolves after CO₂ injection. Reaction rates of other minerals are much smaller than those of quartz and albite. Comparisons of results using TOUGHREACT and PFLTRAN show trivial differences between them.

The net heat extraction and mass flow production rate for CO₂ as working fluid are much larger compared to water as working fluid, indicating supercritical CO₂ as working fluid in EGS reservoirs could enhance heat extraction instead of water as working

fluid. It is also observed that the differences of net heat extraction for CO₂ and water as working fluids decrease with time after 4 years at fully saturated CO₂ conditions. This is explained by more rapid thermal depletion using CO₂ than water, which is also verified by the relatively larger drop of temperature for CO₂ as working fluid compared to water at the late stage of simulation.

The pressure drops between injection and production wells have significant effects on net heat extraction, mass flow rate, and temperature. Generally, large pressure drop could lead to large net heat extraction and mass flow rates at the early and middle stages of simulation. However, after 50 years of CO₂ injection, the net heat extraction for pressure drop of 25 bar is larger than the one for pressure drop of 10, 50, and 100 bar, suggesting the pressure drop of 25 bar between injection and production wells is suitable for heat extraction in EGS reservoirs. The initial salinity could significantly affect net heat extraction and mass flow rate at the early stage of simulation. But the effects of initial salinity on heat extraction and flow rate are very little after 4 years of CO₂ injection. Results of our simulation could provide scientific-based information for EGS reservoir optimization design to enhance geothermal energy extraction and facilitate concomitant CO₂ sequestration.

REFERENCES

- André, L., Audigane, P., Azaroual, M., Menjz, A. (2007), "Numerical modeling of fluid-rock chemical interactions at the supercritical CO₂-liquid interface during CO₂ injection into a carbonate reservoir, the Dogger aquifer (Paris Basin, France)," *Energy Conversion & Management*, **48**, 1782-1797.
- Brown, D. (2000), "A hot dry rock geothermal energy concept utilizing supercritical CO₂ instead of water," *Proceedings of Twenty-Fifth Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California.
- Hammond, G.E., Lichtner, P.C., Lu, C. and Mills, R.T. (2010), "Chapter: PFLTRAN: Reactive flow and transport code for use on laptops to leadership-class supercomputers," Ebook: "Groundwater Reactive Transport Models," Editors: Zhang, F., Yeh, G.T. and Parker, J.C., Bentham Science Publishers, ISBN 978-1-60805-029-1.
- Hammond, G.E. and Lichtner, P.C. (2010), "Field- scale model for the natural attenuation of uranium at the Hanford 300 Area using

- high- performance computing,” *Water Resources Research*, **46**, W09527, doi:10.1029/2009WR008819.
- Lo Ré, C., Kaszuba, J., Moore, J. and McPherson, B.J. (2012), “Supercritical CO₂ in a granite-hosted geothermal system: Experimental insights into multiphase fluid-rock interactions,” *Proceedings of the Thirty-Seventh Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California*.
- Newell, D.L., Kaszuba, J.P., Viswanathan, H.S., Pawar, R.J. and Carpenter, T. (2008), “Significance of carbonate buffers in natural waters reacting with supercritical CO₂: Implications for monitoring, measuring and verification (MMV) of geological carbon sequestration,” *Geophysical Research Letters*, **35**, L23403, doi:10.1029/2008GL035615.
- Palandri, J.L. and Kharaka, Y.K. (2004), “A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling,” *U.S. Geological Survey Open File Report 2004-1068*, Menlo Park, California.
- Perez, R.J. and Boles, J.R. (2005), “An empirically derived kinetic model for Albitization of detrital Plagioclase,” *American Journal of Science*, **305**, 312-343.
- Pruess, K., Oldenburg, C. and Moridis, G. (1999), “TOUGH2 User’s Guide, Version 2.0,” *Report LBNL-43134*, Lawrence Berkeley National Laboratory, Berkeley, California.
- Pruess, K. (2005), “ECO2N: A TOUGH2 fluid property module for mixtures of water, NaCl, and CO₂,” *Report LBNL-57952*, Lawrence Berkeley National Laboratory, Berkeley, California.
- Pruess, K. (2007), “Enhanced geothermal systems (EGS): Comparing water and CO₂ as heat transmission fluids,” *Proceedings of New Zealand Geothermal Workshop, Auckland, New Zealand*.
- Pruess, K. (2008), “On production behavior of enhanced geothermal systems with CO₂ as working fluid,” *Energy Conversion & Management*, **49**, 1446-1454.
- Pruess, K. and Spycher, N. (2010), “Enhanced geothermal systems (EGS) with CO₂ as a heat transmission fluid – a scheme for combining recovery of renewable energy with geologic storage of CO₂,” *Proceedings of World Geothermal Congress, Bali, Indonesia*.
- Rosenbauer, R.J., Koksalan, T. and Palandri, J.L. (2005), “Experimental investigation of CO₂-brine-rock interactions at elevated temperature and pressure: Implications for CO₂ sequestration in deep-saline aquifers,” *Fuel Processing Technology*, **86**, 1581-1597.
- Wan, Y., Xu, T. and Pruess, K. (2011), “Impact of fluid-rock interactions on enhanced geothermal systems with CO₂ as heat transmission fluid,” *Proceedings of Thirty-Sixth Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California*.
- Wigand, M., Kaszuba, J.P., Carey, J.W. and Hollis, W.K. (2009), “Geochemical effects of CO₂ sequestration on fractured wellbore cement at the cement/caprock interface,” *Chemical Geology*, **265**, 122-133.
- Xu, T., Apps, J.A. and Pruess, K. (2004), “Numerical simulation of CO₂ disposal by mineral trapping in deep aquifers,” *Applied Geochemistry*, **19**, 917-936.
- Xu, T., Sonnenthal, E.L., Spycher, N. and Pruess, K. (2006), “TOUGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media,” *Computer & Geosciences*, **32**, 145-165.
- Xu, T., Pruess, K. and Apps, J. (2008), “Numerical studies of fluid-rock interactions in enhanced geothermal systems (EGS) with CO₂ as working fluid,” *Proceedings of Thirty-third Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California*.