Research Article

Evaluation of CO₂-Fluid-Rock Interaction in Enhanced Geothermal Systems: Field-Scale Geochemical Simulations

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Recent studies suggest that using supercritical CO₂ (scCO₂) instead of water as a heat transmission fluid in Enhanced Geothermal Systems (EGS) may improve energy extraction. While CO₂-fluid-rock interactions at “typical” temperatures and pressures of subsurface reservoirs are fairly well known, such understanding for the elevated conditions of EGS is relatively unresolved. Geochemical impacts of CO₂ as a working fluid (“CO₂-EGS”) compared to those for water as a working fluid (H₂O-EGS) are needed. The primary objectives of this study are (1) constraining geochemical processes associated with CO₂-fluid-rock interactions under the high pressures and temperatures of a typical CO₂-EGS site and (2) comparing geochemical impacts of CO₂-EGS to geochemical impacts of H₂O-EGS. The St. John’s Dome CO₂-EGS research site in Arizona was adopted as a case study. A 3D model of the site was developed. Net heat extraction and mass flow production rates for CO₂-EGS were larger compared to H₂O-EGS, suggesting that using scCO₂ as a working fluid may enhance EGS heat extraction. More aqueous CO₂ accumulates within upper- and lower-lying layers than in the injection/production layers, reducing pH values and leading to increased dissolution and precipitation of minerals in those upper and lower layers. Dissolution of oligoclase for water as a working fluid shows smaller magnitude in rates and different distributions in profile than those for scCO₂ as a working fluid. It indicates that geochemical processes of scCO₂-rock interaction have significant effects on mineral dissolution and precipitation in magnitudes and distributions.

1. Introduction

Recent studies suggest that supercritical CO₂ (scCO₂) as a heat transmission fluid in Enhanced Geothermal Systems (EGS) can improve energy extraction compared to conventional water-based EGS [1–3]. We refer to such systems as CO₂-EGS and to EGS with water as a working fluid as H₂O-EGS. Advantages of using CO₂ as a heat transmission fluid include larger expansivity (compressibility) and lower viscosity compared to water; CO₂ is also a poor mineral solvent compared to water [1]. Disadvantages of CO₂ as a working fluid include a lower mass heat capacity than water, reducing its net energy content per unit volume, as well as the propensity for aqueous CO₂ to promote chemical reactions leading to changes in reservoir rock porosity and permeability [4]. However, CO₂-EGS data, as well as comparisons

of CO₂-EGS to H₂O-EGS, are limited. A primary goal of this study is to constrain geochemical reactions induced by CO₂-fluid-rock interactions in EGS reservoirs. An additional goal is to compare geochemical impacts of CO₂-EGS to the geochemical impacts of H₂O-EGS.

Several recent experimental and numerical efforts quantify geochemical reactions associated with CO₂ injection in EGS reservoirs [2, 3, 5–10]. Pruess [2, 3] 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, suggesting that CO₂ offers potential benefits as a working fluid in EGS reservoirs. Rosenbauer et al. [8] experimentally tested CO₂-brine-rock interactions at 120°C and 20–30 MPa. Results suggested that dissolved CO₂ may enhance water-rock interaction and CO₂

sequestration in carbonate minerals. Lo Ré et al. [6] conducted five hydrothermal experiments to evaluate geochemical and mineralogical response of fractured granitic rocks to CO₂ injection at geothermal conditions of at 250°C and 25–45 MPa. Experimental results suggest that precipitation of clay (smectite and illite) may affect reservoir porosity and permeability, and carbonate formation may require extended periods of time. Jung et al. [5] performed reactive transport modeling to study fluid-rock interactions in a typical geothermal system and calibrated the geochemical model by adjusting the reactive surface area to fit the experimental data of mineral dissolution. Na et al. [7] performed laboratory experiments to study CO₂-fluid-rock chemical reactions at high temperatures and pressures in geothermal systems and conducted batch simulations to analyze the experimental data. Wan et al. [9] and Xu et al. [10] simulated geochemical processes of fluid-rock interactions within CO₂-EGS under high pressures and temperatures, and results suggest that significant CO₂ may be stored in EGS reservoirs by mineral trapping by precipitation of carbonate minerals. Xu et al. [11] also performed batch geochemical simulations for three different aquifer lithologies to evaluate long-term CO₂ disposal in deep aquifers. Results suggest that CO₂ sequestration by mineral trapping varies largely with rock type and mineral composition, and porosity decreases 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 suggest that geochemical reactivity with supercritical CO₂ injection was much lower than reactivity with CO₂-saturated water.

Although these experimental and numerical studies address many aspects of geochemical reactions induced by CO₂-fluid-rock interactions in geothermal systems, three-dimensional (3D) geochemical simulations of CO₂-fluid-rock interaction at high temperature and pressure in EGS reservoirs are relatively rare. Therefore, a primary objective of this study is to simulate and evaluate geochemical processes induced by CO₂-fluid-rock interactions at the elevated temperatures and pressures of a CO₂-EGS. A secondary objective is to compare geochemical impacts within a CO₂-EGS to those within an H₂O-EGS. The TOUGHREACT model [12] with the ECO2H module [13] was used to conduct simulations of CO₂-fluid-rock interactions in a CO₂-EGS reservoir. The St. John's Dome CO₂-EGS research site in Arizona was used as a case study example.

2. Material and Methods

2.1. St. John's Dome CO₂-EGS Research Site. St. John's Dome is located along the boundary between Arizona and New Mexico, about half way between the Four Corners area and the Mexican Border. St. John's Dome is part of the Colorado Plateau and covers an area of approximately 1,800 km² ([14]; Rauzi, personal communication, 2013). The dome consists of a broad, asymmetric anticline that trends northwest with an axis that plunges to the northwest and the southeast. The dome is notable for hosting a gas field consisting of

nearly pure CO₂; the Fort Apache, Big A Butte, and Amos Wash members of the Supai Formation (Permian) are the primary CO₂ reservoirs. The caprock above each CO₂-rich zone consists of anhydrite and mudstones [15]; basement consists of Precambrian granite.

Exploration and research of the geothermal potential of St. John's Dome extends back at least into the 1970s. More than 40 wells have been drilled to determine the gas reserves. Bottom-hole temperature measurements have been taken in seven of these wells. Temperature gradients appear to be highest in the south-central portion of the dome; the temperature at a depth of 3 km in this part of the dome is 150°C or greater. Based on identified geothermal resources and large volumes of CO₂, the St. John's Dome is uniquely suitable for developing CO₂-EGS because it greatly reduces the risk and cost of testing and developing the technology.

2.2. 3D Model Setup. We elected to adopt a 5-spot well pattern because of its wide application in oil fields and geothermal reservoirs [3, 9, 17–22]. The resulting 3D model domain with its 5-spot well pattern is illustrated in Figure 1. Due to the symmetry of the 5-spot well pattern, we employed a 1/8 symmetry domain (of the 5-spot pattern) for all simulations (Figure 1). The domain is 500 m in the vertical direction with a layered geological setting, including 100 m thick fractured rock at the middle and 200 m thick granite above and below the fractured rock zone, respectively (Figure 1). The grid cell size is uniform at 70.7 m horizontally (*X* and *Y* directions) and 50 m vertically (*Z* direction). We also implemented a dual-continuum approach at the 100 m thick center of the model domain to represent a typical fractured EGS reservoir.

We collected all publicly-available hydrologic data for wells near St. John's Dome, primarily from files of Arizona Geological Survey. The mean value of measured permeability (0.25 mD) was assigned to all fractured aspects of the model. The MINC (multiple interacting continua) of TOUGH2 code [23] is used to represent matrix-fracture heat transfer with a fracture spacing of 50 m and fracture volume fraction of 2%. Injection and production wells are placed at the bottom of the fractured rock layer with a depth of 275 m from the top of domain and 2000 m from the surface (Figure 1). Assigned initial conditions include hydrostatic pressure and conductive heat flow (temperature gradient 40°C/km), with 20 MPa and 200°C at 275 m depth from the top of the domain. A Dirichlet boundary condition (constant pressure) is assigned to boundaries of injection and production, with a pressure drop of 2.5 MPa between the injection and production wells. For wells, constant pressure is assigned as initial plus 1.25 MPa at the injection well and initial minus 1.25 MPa at the production well. A Neumann condition (no flow) is assigned on all other sides. Details of parameter settings are summarized in Table 1.

2.3. Mineralogical Assemblages in St. John's Dome Field Site. Two core samples of the Precambrian granite from one of the Arizona wells (22-1X State) at Springerville-St. John's CO₂ research site [24] were analyzed using X-ray diffraction

FIGURE 1: Schematic of the 3D numerical model domain with a 5-spot well pattern (1/8 system domain used for all simulations).

TABLE 1: Hydrologic parameters, initial, and injection/production boundary conditions used for 3D simulations of a 5-spot well pattern.

Properties	
Fractured rock permeability	$2.47 \times 10^{-16} \text{ m}^2$ (0.25 mD)
High granite permeability	$9.87 \times 10^{-18} \text{ m}^2$ (0.01 mD)
Fracture spacing	50 m
Fracture volume fraction	2%
Fracture porosity	0.50
Granite porosity	0.08
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	All water
Initial temperature	200°C at the layer of production well with 40°C/km geothermal gradient
Initial pressure	Hydrostatic pressure with 20 Mpa at the layer of production well
Production/injection condition	
Injection/production	707 m
Well distance	
Injection pressure	Initial +1.25 MPa
Injection temperature	50°C
Production pressure	Initial -1.25 MPa

TABLE 2: Mineral assemblages of core samples from Precambrian granite in Arizona well 22-1X State in the St. John's CO_2 field.

Minerals	Minerals composition (Sample 1 at 640.8 m)	Minerals composition (Sample 2 at 647.4 m)
Quartz	50%	45%
Plagioclase	26%	30%
K-feldspar	21%	19%
Biotite	1%	2%
Muscovite	2%	3%
Total	100%	99%

(XRD) at the Energy & Geoscience Institute, University of Utah. The Arizona well 22-1X State is located near the

northern boundary of the St. John's CO_2 field at an elevation of 1949 m at the ground level; the well penetrates the Permian Supai Formation at a depth from 195 m to 628 m below the surface and Precambrian granite below that [14]. The two core samples for Precambrian granite were collected at depths of 640.8 m and 647.4 m. The two samples consist mainly of quartz (45–50%), plagioclase (26–30%), and K-feldspar (19–21%). An average percentage of the mineralogical assemblages of the two samples (Table 2) were used in the simulations. Potential secondary minerals were identified using equilibrium batch modeling, as follows. Firstly, CO_2 was added to the initial formation brine in contact with the primary mineral assemblage, and the saturation indices of all minerals present in the database were calculated and analyzed. Minerals that became supersaturated and have the potential to form under the given conditions were included as secondary minerals. Then, batch models were reexecuted with the new (resulting) mineral assemblage until an equilibrium aqueous solution was reached. The primary mineral assemblage and possible secondary minerals are listed in Table 3; kinetic properties for these minerals are listed in Table 4. The kinetic properties (rate constant, activation

TABLE 3: Chemical composition and initial volume fractions of primary and secondary minerals for geochemical simulations of the St. John's CO₂ field site.

Mineral	Chemical composition	Initial volume fraction of minerals
<i>Primary</i>		
Quartz	SiO ₂	0.475
Oligoclase	Na _{0.77} Ca _{0.23} Al _{1.23} Si _{2.77} O ₈	0.280
K-Feldspar	KAlSi ₃ O ₈	0.200
Annite ^a	KFe ₃ AlSi ₃ O ₁₀ (OH) ₂	0.0075
Phlogopite ^a	KAlMg ₃ Si ₃ O ₁₀ (OH) ₂	0.0075
Muscovite	KAl ₃ Si ₃ O ₁₀ (OH) ₂	0.025
<i>Secondary</i>		
Calcite	CaCO ₃	0.0
Magnesite	MgCO ₃	0.0
Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ , (H ₂ O)]	0.0
Smectite	K _{0.04} Ca _{0.5} (Al _{2.8} Fe _{0.53} Mg _{0.7})(Si _{7.65} Al _{0.35})O ₂₀ (OH) ₄	0.0
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	0.0
Chlorite	Mg _{2.5} Fe _{2.5} Al ₂ Si ₃ O ₁₀ (OH) ₈	0.0
Albite	NaAlSi ₃ O ₈	0.0
Hematite	Fe ₂ O ₃	0.0
Dolomite	CaMg(CO ₃) ₂	0.0
Ankerite	CaMg _{0.3} Fe _{0.7} (CO ₃) ₂	0.0
Dawsonite	NaAlCO ₃ (OH) ₂	0.0
Siderite	FeCO ₃	0.0

^aBiotite is assumed as 50% of Annite and 50% of Phlogopite.

TABLE 4: Kinetic rate parameters of primary and secondary minerals and reactive surface area for the geochemical simulations of the St. John's CO₂ research site.

Mineral	Neutral mechanism		Acid mechanism			Base mechanism			Reactive surface area (cm ² /g)
	log <i>k</i> ^a	<i>E_a</i> ^b	log <i>k</i> ^a	<i>E_a</i> ^b	<i>n</i> ^c	log <i>k</i> ^a	<i>E_a</i> ^b	<i>n</i> ^c	
Primary									
Quartz	−13.99	87.7	—	—	—	—	—	—	9.8
Oligoclase	−11.84	69.8	−9.67	65.0	0.457	—	—	—	9.8
K-feldspar	−12.41	38.0	−10.06	51.7	0.500	−21.2	94.1	−0.823	9.8
Annite ^d	−12.55	22.0	−9.84	22.0	0.525	—	—	—	9.8
Phlogopite	−12.40	29.0	—	—	—	—	—	—	9.8
Muscovite	−13.55	22.0	−11.85	22.0	0.370	−14.55	22.0	−0.220	151.6
Secondary									
Calcite	−5.81	23.5	−0.30	14.4	1.000	—	—	—	9.8
Magnesite	−9.34	23.5	−6.38	14.4	1.000	—	—	—	9.8
Illite ^e	−13.55	22.0	−11.85	22.0	0.370	−14.55	22.0	−0.220	151.6
Smectite	−12.78	35.0	−10.98	23.6	0.340	−16.52	58.9	−0.400	151.6
Kaolinite	−13.16	22.2	−11.31	65.9	0.777	−17.05	17.9	−0.472	151.6
Chlorite	−12.52	88.0	−11.11	88.0	0.500	—	—	—	9.8
Albite	−12.56	69.8	−10.16	65.0	0.457	−15.6	71.0	−0.572	9.8
Hematite	−14.60	66.2	−9.39	66.2	1.000	—	—	—	9.8
Dolomite	−7.53	52.2	−3.19	36.1	0.500	−5.11	34.8	0.500	9.8
Ankerite ^f	−7.53	52.2	−3.19	36.1	0.500	−5.11	34.8	0.500	9.8
Dawsonite	−7.00	62.8	—	—	—	—	—	—	9.8
Siderite	−8.90	62.8	−3.19	36.1	0.500	—	—	—	9.8

Note. Kinetic rate parameters from Palandri and Kharaka [16]; ^alog *k*: 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⁺; ^dset to Biotite; ^eset to Muscovite; ^fset to Dolomite.

FIGURE 2: Simulated heat extraction rate, mass flow rate, temperature, and gas saturation next to production well for scCO₂ (solid line) and water (dash line) as working fluids, respectively.

energy, and power term) of multiple mechanisms (neutral, acid, and base) for primary and possible secondary minerals are taken from Palandri and Kharaka [16]. The reactive surface areas of some minerals (e.g., quartz, oligoclase, albite, K-feldspar, calcite, magnesite, kaolinite, siderite, illite, and smectite) are taken from Xu et al. [11]. Values for other minerals are assumed as 9.8 cm²/g. All geochemical simulations utilize the EQ3/6 thermodynamic database v7.2b (data0.dat; [25]), and all flow aspects are simulated (for 50-year simulation time) using the TOUGHREACT/ECO2H model [12, 26]. A set of batch simulations were conducted first, to obtain initial aqueous solutions that would be in equilibrium with the primary minerals.

2.4. Numerical Models. The TOUGHREACT model [12] with its ECO2H module [13] was used to conduct all geochemical simulations. The TOUGHREACT code was developed to simulate nonisothermal multicomponent reactive fluid flow and geochemical transport by addressing reactive geochemistry with multiphase flow and heat flow [12, 26]. TOUGHREACT has been applied to subsurface thermophysical-chemical processes in various environmental problems and geologic systems. The ECO2H module of TOUGHREACT code is designed for applications to geological sequestration of CO₂ in saline aquifers at high temperature and pressure [13]. The resident equation of state provides an

accurate and comprehensive description of thermodynamics and thermophysical properties of water-brine-CO₂ mixtures to 243°C and 67.6 MPa [19].

3. Results

3.1. Results of Flow and Heat Simulation at St. John's Dome Site. Figure 2 plots net heat extraction rate, mass flow rate, temperature and gas saturation at the gridblock next to the injection, and production wells for the model with scCO₂ as the working fluid. Results for water as a working fluid are also plotted in Figure 2. For the case of scCO₂ as a working fluid, flow containing water only is produced at a rate of ~180 kg/s during the initial stages of simulation. After 0.05 years, the produced water flow rate sharply decreases as the flow rate of produced CO₂ increases, demonstrating the mixture of water and CO₂ produced when scCO₂ has reached the production well. With continuous CO₂ injection and increases in gas saturation at the production well, the produced CO₂ flow rate significantly increases with no water production. The oscillation in mass flow and heat extraction rate at the early stages of simulation (Figure 2) is a simulation artifact. Specifically, this minor oscillation is a numerical response to maintain constant pressure at the wellbore; an absolute constant pressure in a wellbore cannot exist in nature, and to force such in a simulation translates to some oscillatory

FIGURE 3: Simulated 3D profiles of gas saturation and temperature after 30-year injection of scCO₂ as a working fluid.

variability in flows. We adopted fixed wellbore pressure at depth, despite the minor oscillation artifact, because it is a common approach of analysis. The net heat extraction rate is around 120 MW in the initial stage of simulation and decreases to 60 MW after 0.1 years, a trend similar to the produced water flow rate. With increases of produced CO₂ flow rate, the net heat extraction increases to its maximum of 80 MW after 5 years of CO₂ injection. With continuous increase of CO₂ gas saturation at the production well, the net heat extraction decreases to 12 MW after 50 years of CO₂ injection. This is due to more rapid thermal depletion of CO₂ compared to water, associated with the rapid decrease of simulated temperature (Figure 2). The CO₂ saturation next to the injection well becomes 100% after 0.2 years of CO₂ injection. The CO₂ flow breaks through to the production well after 0.06 years of injection and gas saturation continues increasing to 1.0 after 10 years of CO₂ injection. However, the gas saturation decreases from 1.0 to 0.6 at the production well after 20 years of CO₂ injection, demonstrating possible CO₂ leakage to upper-lying layers (Figure 3). The temperature next to the injection well decreases from the initial temperature of 200°C to the injection temperature of 50°C. The temperature next to the production well remains constant at the initial temperature of 200°C until around 2 years of CO₂ injection and then drops to 65°C after 50 years of CO₂ injection.

Figure 3 plots simulated 3D profiles of gas saturation and temperature after 30 years of scCO₂ injection (as a working fluid). The gas saturation at the layer of injection/production well decreases from 1.0 to 0.5 toward the production well after 30 years. The gas saturation varies from 0.2 to 0.5 in the area of upper-lying layers after 30 years, demonstrating that simulated CO₂ leakage occurs and CO₂ breakthrough in caprock may constitute a leakage risk. The gas saturation is around 0.5 in the layer just below the injection/production well (Figure 3). The 3D temperature profile exhibits a similar trend as the gas saturation profile, which increases from 50°C at the injection well to 80°C at the production well (Figure 3), similar to the results in Figure 2. The temperature drop also occurs in the layers just above and below the injection/production layer, associated with large gas saturation in that area.

For water as a working fluid, the mass flow rate next to the production well decreases from 100 kg/s at the initial stage of simulation to 53 kg/s after 50 years of water injection (Figure 2), which is less than the 180 kg/s initial rate and less than the 150 to 250 kg/s of the produced CO₂ flow rate at the late stage of simulations with scCO₂ as a working fluid. A possible explanation for this phenomenon is the lower viscosity of scCO₂ compared to water. The net heat extraction for water as a working fluid has similar trends

FIGURE 4: Simulated 3D profiles of dissolved CO_2 mass fraction in aqueous phase and pH values after 30-year injection of scCO_2 as a working fluid.

for the produced water flow rate, which also decreases from 80 MW at the initial stage to 10 MW after 50 years (Figure 2). The net heat extraction rate for scCO_2 as a working fluid varies from 12 to 180 MW during the simulation period and is much larger than the rate for water as a working fluid, indicating that scCO_2 as a working fluid could enhance heat extraction compared to water, at least for a generic 5-spot well pattern.

3.2. Results of Geochemical Simulation at St. John's Dome Site.

Figure 4 plots simulated 3D profiles of aqueous CO_2 mass fraction and pH values after 30 years. Figures 5 and 6 illustrate simulated 3D profiles of changes of mineral abundances (in volume fraction) for selected primary minerals (oligoclase and quartz) and secondary minerals (calcite and illite). From the beginning of scCO_2 injection, scCO_2 dissolution in water increased the dissolved CO_2 concentration and lowered pH values (compared to the initial pH value of 5.4) (Figure 4). The pH values are artificially set to 0 if the saturation in gas phase is 1.0. The dissolved CO_2 and lowered pH values induced dissolution of primary minerals and precipitation of secondary minerals. Aqueous CO_2 is observed at the upper- and lower-lying layers (Figure 4), which exhibits larger dissolved CO_2 mass fractions than values at the injection/production layer after 30 years. A reverse trend is

associated with the gas saturation distribution (Figure 3), indicating that more CO_2 dissolves in the aqueous phase with lower gas saturation in upper- and lower-lying layers. The pH values in the injection/production layer are smaller than the initial pH value of 5.4 and increase toward the production well (Figure 4), which is similar to the pattern of gas saturation (Figure 3). The higher the gas saturation, the lower pH values, in general.

The primary mineral oligoclase dissolves from the beginning of CO_2 injection. As indicated by Figure 5, a general trend of more dissolution in the upper-lying layers and the layer just below the injection/production layer is observed after 30 years of CO_2 injection. We infer this to be because water is produced gradually from the production well while supercritical CO_2 (gas phase) spreads from the injection well toward the production well, and no chemical reactions occur between scCO_2 (nonaqueous CO_2) and minerals. The primary mineral quartz may precipitate or dissolve after 30 years (Figure 5). The quartz slightly dissolves in water-dominated areas and precipitates in CO_2 -laden areas (Figure 5). We infer this to be because the lower pH values in areas reached by CO_2 result in precipitation of quartz; pH values approaching 5.4 in the water-dominated area lead to dissolution of quartz. The distribution of quartz precipitation has similar patterns and characteristics to the mineral oligoclase. The more

FIGURE 5: Simulated 3D profiles of changes of mineral abundance (in volume fraction) for primary minerals (oligoclase and quartz) after 30-year injection of scCO_2 as a working fluid.

precipitation of quartz occurs within the upper-lying layers and the layer just below injection/production layer (Figure 5).

Calcite precipitates after 1 year of CO_2 injection (figure not shown). The calcite precipitation distribution also shows similar patterns to the oligoclase dissolution profile. More calcite is precipitated in the upper-lying layers and the layer just below injection/production layer after 30 years (Figure 6) than the injection/production layer, tracking the distribution of dissolved CO_2 in the aqueous phase (Figure 4) and CO_2 in gaseous phase (Figure 3). Relatively large amounts of illite precipitation also occur in the same areas with large amounts of calcite precipitation, also tracking aqueous phase CO_2 . The characteristics and distributions of dissolution or precipitation for other minerals (e.g., albite, K-feldspar, and siderite) are similar to trends for oligoclase, calcite, and illite (figures not shown).

Figure 7 describes the cumulative CO_2 sequestered by carbonate mineral precipitation for scCO_2 as a working fluid after 30 years. The total CO_2 sequestered by carbonate precipitation is around $1.5\text{--}3.0\text{ kg/m}^3$ in the upper-lying layers, which is much larger than the value of 0.2 kg/m^3 at the injection/production layer. The 3D distribution of total CO_2 sequestered is identical to the amount consumed by calcite precipitation (Figure 6) and to the dissolved aqueous CO_2 amount (Figure 6) after 30 years of CO_2 injection. This

relationship is consistent with scCO_2 in the gas phase mainly occupying the layer of injection/production wells (Figure 4) and the two phases of water-gas mixtures exist in the area of the upper-lying layers after 30 years, resulting in more dissolved CO_2 in these areas (Figure 3). Therefore, more dissolution and precipitation occur in the upper-lying layers.

To compare the effects of scCO_2 as a working fluid (to water) on chemical interactions, we also simulated the 3D geochemical processes at St. John's Dome Site for water as a working fluid for 50 years. Figure 8 plots simulated pH values and changes of mineral abundances (in volume fraction) for primary mineral (oligoclase) after 30 years for water as a working fluid. The simulated pH values for water as a working fluid increase from the initial value of 5.4 (Figure 8), which decrease for scCO_2 as a working fluid (Figure 4). The dissolution of mineral oligoclase for water as a working fluid (Figure 8) shows smaller magnitude in rates and different distributions in profile than the ones for scCO_2 as a working fluid (Figure 5). The more dissolution of oligoclase occurs in the area above the injection well, and the area close to the production well for water as a working fluid but more dissolution of oligoclase is simulated in the area above the injection/production layer for scCO_2 as a working fluid. Other primary and secondary minerals also exhibit significantly different dissolution or precipitation rates and

FIGURE 6: Simulated 3D profiles of changes of mineral abundance (in volume fraction) for secondary minerals (calcite and illite) after 30-year injection of scCO₂ as a working fluid.

FIGURE 7: Simulated 3D profile of cumulative CO₂ sequestered (kg/m³) by carbonate mineral precipitation after 30-year injection of scCO₂ as a working fluid.

patterns for water as a working fluid (figures not shown) from the ones for scCO₂ as a working fluid. It indicates that the geochemical processes of scCO₂-rock interaction have significant effects on mineral dissolution and precipitation in magnitudes and distributions.

4. Conclusions

A 3D model of the St. John's Dome CO₂-EGS site was employed to simulate flow, heat extraction, and geochemical processes induced by CO₂-fluid-rock interactions. Net heat

FIGURE 8: Simulated 3D profiles of pH values and changes of mineral abundance (in volume fraction) for primary mineral oligoclase after 30-year injection of water as a working fluid.

extraction and mass flow production rates for scCO_2 as a working fluid were larger (X to Y) compared to water (A to B) as a working fluid, indicating scCO_2 as a working fluid may enhance EGS heat extraction (consistent with Pruess [2, 3]). Simulated CO_2 saturation suggests that CO_2 breakthrough in caprock may constitute a leakage risk, at least for the specific case of the St. John's Dome CO_2 -EGS research site. Simulations also suggest that more aqueous CO_2 accumulates within the upper- and lower-lying layers than within the injection/production layer, decreasing pH values and promoting dissolution and precipitation of minerals in the upper- and lower-lying layers of the system. Precipitation of carbonate minerals in the upper-lying layers suggests favorable CO_2 storage (with respect to mineral trapping) in EGS reservoirs. Dissolution of oligoclase for water as a working fluid shows smaller magnitude in rates and different distributions in profile than those for scCO_2 as a working fluid. It indicates that geochemical processes of scCO_2 -rock interaction have significant effects on mineral dissolution and precipitation in magnitudes and distributions. Results of this study improve understanding of geochemical processes within CO_2 -EGS reservoirs and provide implications for enhanced energy extraction and geological CO_2 sequestration.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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