

GEOCHEMICAL MODELING OF WATER-ROCK-PROPPANT INTERACTIONS

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ABSTRACT

Enhanced geothermal system (EGS) reservoir fracture creation and management may require the use of proppants to maintain fracture conductivity. The most commonly used proppants, which remain in hydraulically created fractures to keep them open, include silica sand, ceramic, and sintered bauxite. In geothermal systems, proppant will need to withstand high temperatures, acidified fluids, acid treatments, and cleanouts while maintaining the porosity and permeability of the fracture. Geochemical modeling of water-rock-proppant interactions was conducted in conjunction with static experiments to extrapolate experimental observations to the reservoir scale. PHREEQC was used to examine the chemical stability of silica and bauxite proppants in equilibrium with fluids of varying composition. TOUGHREACT was used to model one dimensional flow of these fluids through a granite reservoir with fractures filled with silica or bauxite proppant. The modeled results indicate that under certain conditions, proppant can either dissolve or act as a nucleation site for mineral precipitates.

INTRODUCTION

In the oil and gas industry, hydraulic fracturing is often accompanied by the addition of proppants. Proppants are sized particles that are added to fracturing fluids and remain in the fracture to physically hold the newly created fracture open while maintaining conductivity within the fracture. A variety of proppants are available, and the most commonly used proppants consist of silica sand, ceramic and resin coated sands, and bauxite. In enhanced geothermal systems (EGS), proppant will need to withstand high temperatures, acidified fluids, acid treatments, and cleanouts while maintaining the porosity and permeability of the fracture. However, proppant particles may act as nucleation sites and promote precipitation, or they may dissolve,

consequently affecting fracture performance. Thus, the performance of proppants in geothermal reservoirs must be understood to avoid costly mistakes in the creation and maintenance of EGS reservoirs. The goal of this investigation is to develop improved methods for maintaining permeable fracture volumes in EGS reservoirs by experimentally evaluating the performance of proppants (natural and manufactured) under conditions found within geothermal environments and determining the effects of mineral deposition and dissolution on propped fractures.

Previous Studies

A study in the Northeast German Basin used high-strength ceramic proppant in a well at 4080-4190m depth and 140°C (Legarth et al, 2003). Propped fractures were created, and inflow performance of well was significantly enhanced. Even so, post-fracture productivity was not as high as predicted. The possible reasons given for this discrepancy are chemical and mechanical processes during shut-in or undersized and poorly connected fractures.

Previous studies from the oil and gas industry have reported that sintered bauxite proppant is resilient under high stress environments (Cooke, 1977). When formation stresses are high, these proppants deform, rather than crush. This deformation allows for the increase of contact area between proppant grains or between proppant and the wall rock. Quartz sand has been shown to crush, decreasing porosity and permeability in the fracture (Cooke, 1977). Significant conductivity losses were reported after flow-through testing with sintered bauxite between sandstone at temperatures between 93 and 287°C (Weaver et al., 2009). These losses were partially attributed to geochemical reactions of the fluid, proppant, and formation rock.

McLin et al. (2010) and Brinton et al. (2011) show dissolution of proppant and precipitation of minerals in static experiments. Proppant and a proppant-

granite mixture were reacted with various fluids for up to two months at 200-230°C. Dissolution textures were observed on the surface of the bauxite proppant in several experiments. The precipitated minerals included aluminosilicates (possibly wairakite), zeolites, aluminum oxides/hydroxides, and amorphous silicates. The main mechanisms for precipitation of the minerals were related to the experimental methodology. Fluid leakage concentrated the dissolved components in solution, and cooling the reactor for extended periods of time allowed lower temperature mineral assemblages to become stable and precipitate.

BATCH MODEL SETUP

The bauxite proppant consists mainly of corundum (Al₂O₃). The stability of corundum was examined using Geochemist's Workbench (Bethke, 2008) with the Lawrence Livermore National Laboratory (LLNL) database and PHREEQC (Parkhurst and Appelo, 1999) with the LLNL and THERMODDEM (TDEM) databases. For these models, corundum is dissolved when equilibrated with deionized water. The saturation of gibbsite, boehmite, and diasporite were calculated for temperatures ranging from 0 to 300°C.

PHREEQC was used to model batch equilibrations of fluid with proppant and granite. The LLNL database was used. These simulations were constructed to model the experiments conducted by McLin et al., 2010 and Brinton et al., 2011. Deionized water and fluid with a composition based on production fluid from Raft River well RRG-7 were reacted with granite and proppant. Simulations were run for both quartz and corundum proppant. Temperatures between 100 and 250°C were used for these equilibrations. Outputs include pre- and post-reaction fluid chemistries and mineral saturation indexes.

FLOW MODEL SETUP

The flow simulations were carried out using the non-isothermal reactive geochemical transport code TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2004). This code was developed by introducing reactive chemistry into the framework of the existing multi-phase fluid and heat flow code TOUGH2 V2 (Pruess et al., 1999, see also <http://www-esd.lbl.gov/TOUGHREACT/>). Interactions between mineral assemblages and fluids can occur under local equilibrium or kinetic rates. The gas phase can be chemically active. Precipitation and dissolution reactions can change formation porosity and permeability, as well as modify the unsaturated flow properties of the rock. This simulator can be applied

to 1-, 2-, and 3-dimensional porous and fractured media with physical and chemical heterogeneity. It can handle any number of species present in the liquid, solid, and gaseous phases.

Fluid and Heat Flow Conditions

The geometry and fluid and heat flow conditions are modeled after those described in Xu and Pruess (2004) and similar to those used by McLin et al (2006). A one-dimensional MINC (multiple interacting continua) model was used to represent the fractured rock. The MINC method can resolve "global" flow and diffusion of chemicals in the fractured rock and its interaction with "local" exchange between fractures and matrix. Details on the MINC method for reactive geochemical transport are described by Xu and Pruess (2001). In the simulations we considered interactions with: 1) a zone representing the relatively impermeable, unaltered host rock and 2) altered host rock containing fractures filled with either corundum or quartz proppant. Granite was used as the host rock for these models. The flow distance was 698 meters, and the simulation monitored changes in temperature, fluid chemistry, porosity, permeability, and mineral volume fractions through $t = 7$ years. The parameters used in the models are shown in Table 1. Density = 2650 kg*m⁻³, heat capacity = 1000 J*kg⁻¹K⁻¹, and diffusivity = 10⁻⁹ m²s⁻¹ were used for all zones. The cubic law was used to define the porosity-permeability relationship in both zones (Xu et al., 2004). The model generates changes in porosity and permeability based on changes in mineral abundances.

Table 1. Hydrologic and thermal parameters of rocks used in the models

Parameters	Fracture	Granite
Volume (m ³)	0.1	0.9
Permeability (m ²)	1.0E-13	2.0E-18
Porosity	0.30-0.50	0.02
Thermal Conductivity (W* m ⁻¹ K ⁻¹)	2.9	3.0
Tortuosity	0.3	0.1

Mineralogical Conditions

The mineralogical composition of the reservoir rock is an estimated composition of granite. The fractures were given the porosity, permeability, and tortuosity of a typical sandstone (as used in Xu et al., 2007). A higher porosity situation was also considered for the bauxite propped fracture. The type of proppant used in the simulation determined the mineralogy of the fracture zone. The bauxite proppant was simulated as mostly corundum with a few mineral contaminants,

such as quartz, calcite, and clay minerals. Mineralogical compositions of the host rock and fractures are presented in Table 2.

Table 2. Mineralogical composition of the granite used in the simulations. A temperature of 200°C was used for the initial rock temperature in the simulations.

Mineral	Granite	Fracture (bauxite proppant)	Fracture (quartz proppant)
Quartz	0.22	0.06	0.90
Potassium Feldspar	0.22		
Chlorite	0.10	0.01	0.01
Illite	0.10	0.01	0.01
Calcite	0.03	0.04	0.05
Smectite		0.03	0.03
Anorthite	0.29		
Annite	0.06		
Amorphous Silica			
Corundum		0.85	

Mineral Kinetic Rates and Parameters

Mineral dissolution and precipitation are considered under kinetic constraints, with the exception of corundum, gibbsite, boehmite, and diaspore. A general kinetic rate expression is used in TOUGHREACT (Xu et al., 2004), or

$$r_m = \pm k_m A_m a_{H^+}^n |1 - Q_m/K_m| \quad (1)$$

where m is the mineral index, r_m is the dissolution/precipitation rate, (positive for dissolution, negative for precipitation), k_m is the rate constant (moles per unit mineral surface area and unit time) which is temperature-dependent, A_m is the specific reactive surface area per kg of H_2O , a_{H^+} is the activity of H^+ , and n is an empirical reaction order accounting for catalysis by H^+ in solution. K_m is the equilibrium constant for the mineral-water reaction written for the destruction of one mole of mineral m , Q_m is the ion activity product. The temperature dependence of the reaction rate constant can be expressed as:

$$k = k_{25} \exp[-E_a/R(1/T-1/298.15)] \quad (2)$$

where E_a is the activation energy, k_{25} is the rate constant at 25°C, R is the universal gas constant, and T is absolute temperature. Table 3 shows the parameters used in the kinetic rate expression.

Water Chemistry

Initial fluid compositions within the fracture and host rock were calculated by equilibrating production fluid from Raft River well RRG-7 with granite at 200°C. The injection fluid was taken from analysis of production fluid from Raft River well RRG-7 (Table 4). The injectate composition was not allowed to change over time.

Table 3. List of kinetic rate parameters used in Eqns. (1) and (2) for minerals considered in the present paper (Palandri and Kharaka, 2004 and Xu et al., 2007). The first line indicates dissolution parameters and the second line precipitation parameters; the same values were used for both where only one line is shown. Only the neutral mechanism was considered.

Mineral	A (cm ² /g)	Neutral Mechanism	
		k ₂₅ (mol m ⁻² s ⁻¹)	E _a (kJ/mol)
Quartz	9.1	1.023E-14	35
Am. Silica	9.1	4.900E-13	76
	9.1	3.800E-10	49.8
K-feldspar	9.1	3.890E-13	38
Anorthite	9.1	7.586E-10	17.8
Smectite	108.7	1.660E-13	35
Illite	108.7	1.660E-13	35
Annite	9.1	2.512E-15	66.20
	9.1	6.457E-07	18.98
Calcite	9.1	6.457E07	62.76
	9.1	3.020E-13	88

Table 4. Composition of the reservoir at 200°C, the temperature used in the simulations, and injection fluid composition at 109°C based on analysis of produced fluid from Raft River well RRG-7.

Chemical Component	Reservoir (mol/kg)	Injection (mol/kg)
SiO ₂	3.549E-3	8.694E-3
Fe ²⁺	1.130E-8	6.689E-9
AlO ₂ ⁻	5.986E-4	1.185E-5
Na ⁺	5.849E-2	3.701E-2
K ⁺	2.617E-3	6.317E-3
Ca ²⁺	8.424E-3	8.697E-3
Mg ²⁺	2.393E-4	2.188E-5
Cl ⁻	9.368E-2	1.229E-1
HCO ₃ ⁻	4.082E-5	2.014E-3
SO ₄ ⁻	3.279E-6	5.696E-3
pH	6.56	7.82

RESULTS

Tables 5.1-3 show the saturation of gibbsite, boehmite, and diaspore from 0°-300°C. None of the aluminum oxides or hydroxides are significantly saturated at 200 to 300°C. These models are consistent with the observed experimental results (Brinton et al., 2011) at 230°C showing dissolution of the corundum proppant.

Table 5.1. Gibbsite saturation for 0-300°C

T (°C)	Log Q/K (GWB LLNL)	Log Q/K (PHREEQC LLNL)	Log Q/K (PHREEQC TDEM)
0	3.2575		
25	2.7316	1.41	1.41
60	2.0956	0.87	0.91
100	1.4791	0.28	0.41
200	0.2924	-1.10	-0.56
300	-0.5648	-2.34	

Table 5.2. Boehmite saturation for 0-300°C

T (°C)	Log Q/K (GWB LLNL)	Log Q/K (PHREEQC LLNL)	Log Q/K (PHREEQC TDEM)
0	1.2512		
25	1.0958	1.60	1.52
60	0.9109	1.23	1.23
100	0.7324	0.75	0.95
200	0.3811	-0.61	0.41
300	0.1083	-2.04	

Table 5.3. Diaspore saturation for 0-300°C

T (°C)	Log Q/K (GWB LLNL)	Log Q/K (PHREEQC LLNL)	Log Q/K (PHREEQC TDEM)
0	2.2359		
25	1.9402	2.00	2.28
60	1.5942	1.58	1.90
100	1.2688	1.04	1.53
200	0.6588	-0.42	0.82
300	0.2186	-1.92	

PHREEQC predicted supersaturation of several minerals in simulations with both corundum and quartz proppant at 200°C. These minerals included anthophyllite, antigorite, talc, tremolite, grossular-andradite, and several zeolites. At lower temperatures, these minerals become under-saturated with the exception of the zeolites. The zeolites become more supersaturated in the 100°C simulations. Because the water to rock ratio was low

for these simulations, the initial minerals present dissolved to saturation at each temperature.

TOUGHREACT flow models predicted declines in porosity and permeability over a short time for the quartz proppant filled fractures. The quartz proppant served as a nucleation site for amorphous silica, calcite, and minor quartz, illite, and smectite. Figure 1 shows the porosity of the quartz sand propped fracture. In the simulation with bauxite proppant and 30% porosity, nothing precipitated or dissolved in the fracture. There was minor dissolution and precipitation of minerals in the granite. However, when porosity was increased to 50%, the corundum dissolved and re-precipitated as diaspore in the first 10 meters of the flow path (Fig. 2). The increased volume of diaspore led to the decline in porosity and permeability. There is minor dissolution and precipitation of other minerals, but these reactions do not seem to significantly affect the porosity and permeability of the propped fracture.

DISCUSSION

Although supersaturation of several minerals, such as grossular, talc, and antigorite, is predicted with batch equilibrations at 200°C, these minerals are not positively identified in the experiments conducted by Brinton et al. (2011). Even if these minerals are not positively identified, they might be present. The concentration of magnesium in solution is so low that the amount of magnesium silicate minerals precipitated may be very minute. Also, kinetic precipitation of these minerals may be slow. The minerals may not precipitate within the time frame of the experiment. Brinton et al. (2011) reports that precipitated zeolites are identified in trial 5, along with aluminum oxides/hydroxides and amorphous silicates in trials 3 and 5. Fluid leakage and prolonged cooling of the reaction vessels probably allowed the precipitation of these minerals. The lower temperature simulations confirm that the temperatures of the reactors were probably much lower than 200°C when these minerals precipitated. In recent static experiments with modified methods to prevent leakage, dissolution of the bauxite proppant is observed, along with possible minor dissolution of the granite at 230°C (Brinton et al., 2011). In flow models where the reservoir was 200°C, there was no dissolution of corundum when the porosity was 30% in the bauxite propped fracture. At a higher water to rock ratio (porosity of 50%), corundum dissolved and re-precipitated as diaspore. This reaction occurred in the cooler part of the flow path where injection had lowered the temperature.

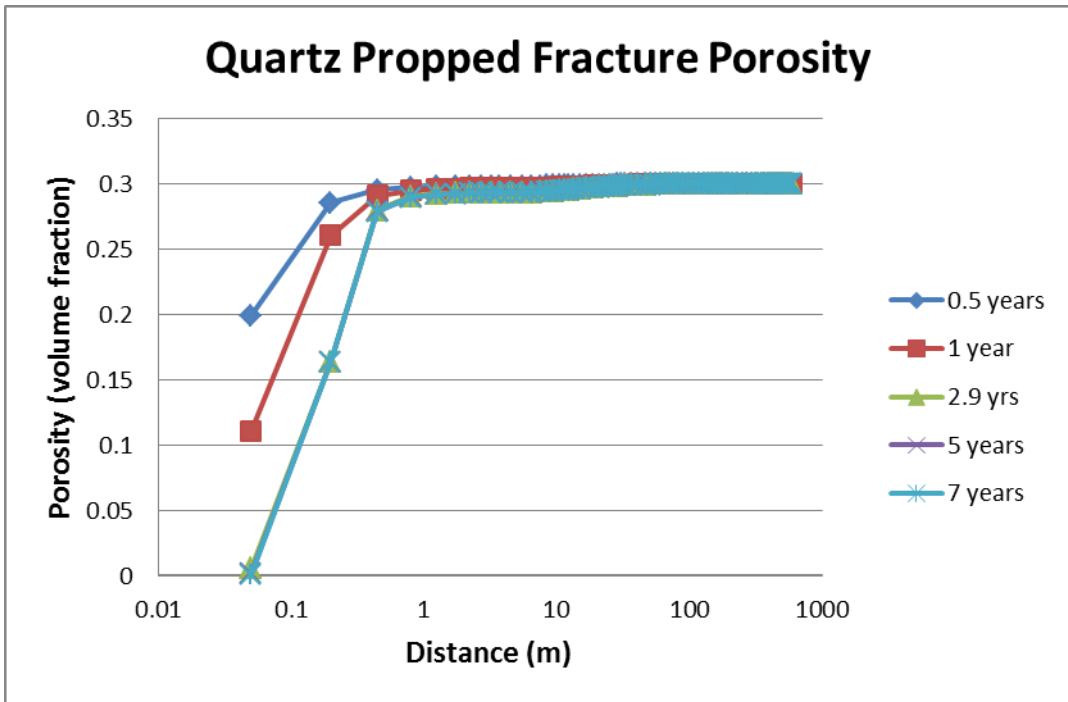


Figure 1. Porosity along the flow path (quartz sand propped fracture) at $t = 0.5$ to 7 years. Initial porosity for the entire flow path (at $t=0$) is 30%.

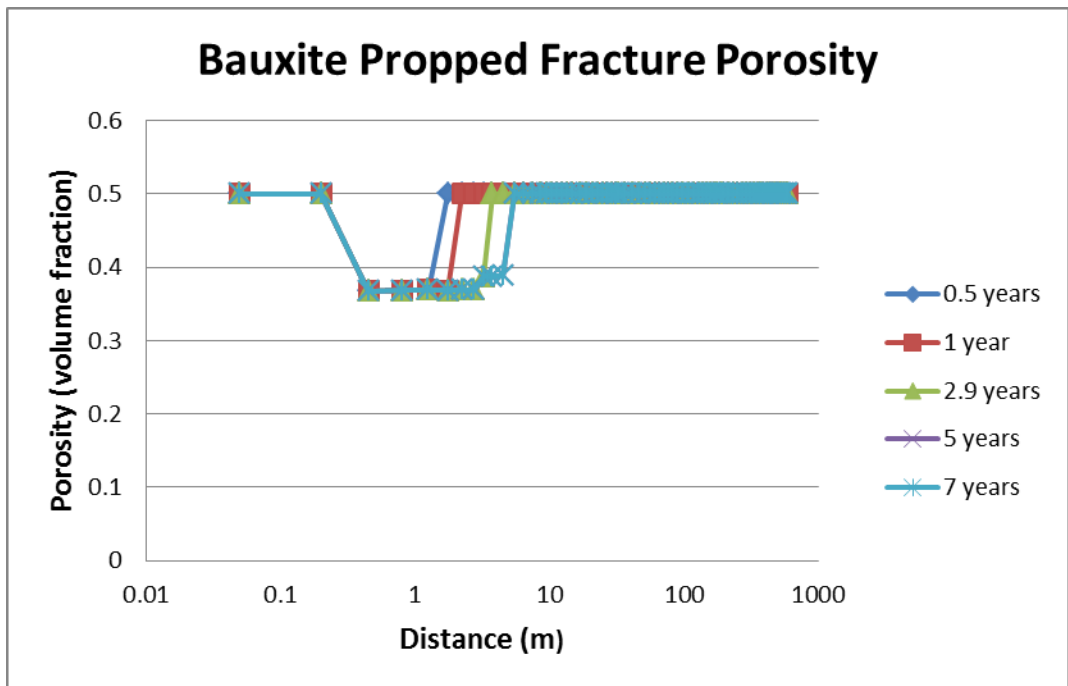


Figure 2. Porosity along the flow path (sintered bauxite propped fracture) at $t = 0.5$ to 7 years. Initial porosity for the entire flow path (at $t=0$) is 50%.

In static experiments conducted with Raft River geothermal fluid, granite, and quartz sand proppant at 230oC, the quartz proppant had dissolved (Brinton et al., 2011). No precipitation was observed on the

proppant or granite after these experiments. In flow simulations with quartz proppant, mineral precipitation decreases fracture porosity and permeability in the first few meters of the flow path.

This precipitation also was predicted in the cooler part of the flow path.

CONCLUSIONS

It is possible that proppants will be 1) chemically stable, 2) dissolve and re-precipitate, or 3) serve as nucleation sites in propped fractures under different chemical conditions. Future TOUGHREACT simulations will investigate the chemical stability of quartz and bauxite proppants under pH modified conditions, with different reservoir and injection temperatures, and with different injection fluid chemistries. These simulations, along with future experiments, will make for better predictions of in-situ chemical stability of proppants in geothermal reservoirs.

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