CHEMICAL STIMULATION IN NEAR-WELLBORE GEOTHERMAL FORMATIONS: SILICA DISSOLUTION IN THE PRESENCE OF CALCITE AT HIGH TEMPERATURE AND HIGH pH

Peter Rose[1], Tianfu Xu[2], Katie Kovac[1], Mike Mella[1], and Karsten Pruess[2]

[1]Energy and Geoscience Institute at the University of Utah
423 Wakara Way Suite 300
Salt Lake City, Utah, 84103 USA
prose@egi.utah.edu
[2]Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California,
1 Cyclotron Road, Berkeley, CA 94720

ABSTRACT

Chemical stimulation was investigated in the laboratory as an alternative to hydraulic stimulation for increasing well injectivity and near-wellbore permeability in geothermal reservoirs. Calcite and silica dissolution rates were measured in a high-temperature flow reactor in the presence of a chelating agent NTA and at high pH. Results indicate that calcite and silica dissolution rates each increase with pH and flow rate. The mineral dissolution processes within the laboratory flow reactor were simulated using a 1-D TOUGHREACT reactive transport model.

INTRODUCTION

As a means of dissolving near-wellbore calcite and of dissolving calcite scale in wellbores, chemical treatment is commonly accomplished by injecting strong mineral acids from the wellhead (Lund et al., 1975). At high geothermal temperatures, however, mineral acids risk corroding steel casings. Acids injected from the surface also tend to enter the formation via the first fluid entry zone, dissolving first-contacted minerals aggressively while leaving much of the rest of the wellbore untreated. Whereas steel casings can usually be protected during acid stimulation by using corrosion inhibitors (except at temperatures approaching or exceeding $300^{o}C$), controlling the reactivity of the strong mineral acid towards calcite dissolution is a more challenging problem.

An alternative to acid treatment is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA) (Fredd and Fogler, 1998). Such chelating agents have the ability to chelate, or bind, metals such as calcium. Through the process of chelation, a calcium ion would be solvated by the chelating agent, allowing the calcite to be transported either to the surface by flowing the well or further into the formation by injecting into the well. The rate of calcite dissolution using chelating agents is not as fast as is the rate of calcite dissolution using strong mineral acids. The lower dissolution rate means that the chelating agent will be able to take a more balanced path and more evenly dissolve calcite along the wellbore and in all available fractures, rather than following the first fluid entry zone and leaving the rest of the wellbore relatively untouched.

The current state-of-the-art method for chemically removing wellbore silica scale is through HF treatments, which are expensive and hazardous. Laboratory data indicate, however, that aqueous solutions at high pH can dissolve wellbore silica and near-wellbore formation silica and quartz reasonably well and at much lower cost than HF treatments. What has prevented geothermal operators from using caustic solutions in the past is the fear of calcite deposition, which is strongly favored at high pH. Our laboratory studies have indicated that calcite is dissolved rather than precipitated at high pH in the presence of chelating agents. This suggests that thermally stable chelating agents at high pH can provide the basis for an affordable and effective mineral dissolution approach.

EXPERIMENTAL APPROACH

The High-Temperature Laboratory Flow Reactor

A schematic drawing of the high-temperature flow reactor is shown in Figure 1. The design and fabrication of this reactor has been previously described (Mella et al., 2006).
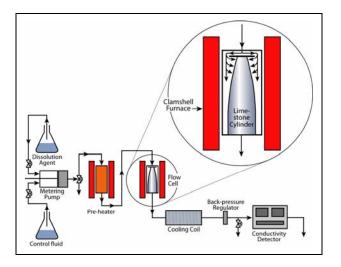
Figure 1. Schematic drawing of the high-temperature flow reactor.

Calcite Dissolution

Tracer Testing of the Reactor

As shown in Figure 1, the flow-reactor was originally designed to allow for the reactant to flow over the surface of a limestone core, with diffusion into and out of the core. But most of the reactant volume simply flowed over the core without making intimate contact with the limestone. Modifications were therefore made to the reactor design to force the reactant solution through the core's pore space. This was achieved by cementing the core to the inside of the reactor cell using a high-temperature silicon adhesive.

To investigate flow patterns through the newly redesigned dissolution reactor, several tests were carried out using real-time tracer detection. In each test, 25 µL of a 100-ppm fluorescein solution was injected into the reactor as a slug via a sample loop. Helium-sparged deionized water was used as the carrier fluid to force the tracer slug through the limestone core. A fluorescence detector was connected after the back pressure regulator and the tracer data were recorded on a computer in real time. The data from each experiment were plotted as tracer response versus time. Each test was repeated several times to ensure quality.

In the first experiment (see Figure 2), the reactor was loaded with an uncemented limestone core and maintained at a temperature of 24°C as water with the tracer slug was allowed to flow through it at a rate of 1 ml/min. The core has a diameter of 0.995 inches and the reactor has an internal diameter of 1.01 inches. From the shape of the tracer response in Figure 2, the flow was assumed to pass almost exclusively around the core within the 0.015 inches of clearance between the core and the reactor, with some undetermined amount of diffusion into and out of the core and/or dispersion through the relatively stagnant regions of the reactor.
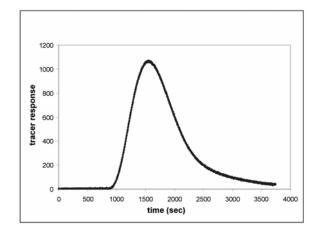

Figure 2. Tracer response in a test of the flow reactor at 24°C and 1 ml/min when an uncemented core was present.

In the subsequent experiment, the reactor/core assembly was modified in order to inhibit flow between the limestone core and the inner surface of the reactor, thus forcing the flow through the pore space within the core. In these experiments the limestone core was covered with a high-temperature/high-strength silicone adhesive before sliding it into the reactor. The adhesive was allowed to cure overnight at a temperature of 32°C.

The tracer experiment was then repeated (see Figure 3). A maximum-tracer response was observed at approximately the same time, but with much lower resolution and with the tracer appearing to be produced in pulses, indicating multiple channeling through the limestone core.
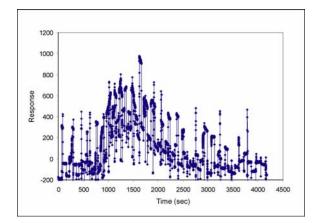

Figure 3. Tracer response in a flow test of the reactor at 24°C and 1 ml/min when the limestone core was bonded to the interior of the reactor.

Having redesigned and evaluated the flow reactor, the next step was to test the various candidate dissolution reagents under conditions that simulate a geothermal reservoir. The obtained data can then be compared to the output of the numerical simulation experiments described below in order to determine how accurately the 1-D reactive transport model simulates the laboratory data.

Silica Dissolution

A preliminary study of silica dissolution at high temperature and high pH was initiated using the flow reactor shown in Figure 1. The limestone rod was replaced with 6-mm glass beads, which served as a proxy for amorphous silica. The temperature ranged between $150^{o}C$ and $300^{o}C$ and the flow rate was 10 ml/min. The injection water had a pH of 14, which was achieved by adding NaOH. Shown in Figure 4 is a plot of silica dissolution as a function of temperature under these conditions.
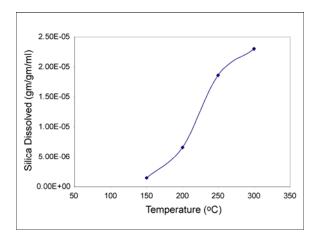

Figure 4. Total silica dissolution in the flow reactor at pH 14 between $150^{o}C$ and $300^{o}C$. Each point on the curve shows the mass of silica dissolved divided by the initial mass and the total solution volume that flowed through the reactor during a 2-hour period.

NUMERICAL SIMULATION STUDY

The 1-D Reactive-Transport Model

A 1-D model using TOUGHREACT was developed in order to simulate mineral dissolution within the benchtop flow reactor under varying conditions of pH, temperature, pressure, flow rate and fluid chemistry. Thermodynamic and kinetic data (as known) for the various mineral dissolution processes are input into the model. Experimental data are then compared to model outputs and the model is calibrated as necessary to match the data. Such an approach will ultimately lead to improved forward-modeling of mineral dissolution in geothermal

formations where operational parameters are more complex and varied.

Calcite Dissolution

Simulation of calcite dissolution at pH 12 in a solution of the chelating agent nitrilotriacetate (NTA) and at various flow rates is shown in Figure 5. The curves show the amount of calcite dissolved along the length of the reactor and over a range of flow rates. Each curve represents an experiment for 1.5 days at a temperature of $21^{o}C$.
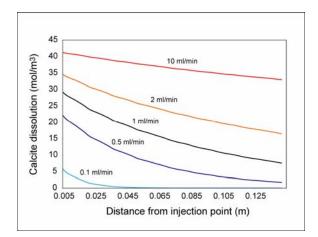

Figure 5. Calcite dissolution after 1.5 days in an NTA solution at pH 12 vs. distance along the flow reactor. The flow rate was varied between 0.1 and 10 ml/min.

Likewise, Figure 6 shows a simulation of calcite dissolution along the reactor length for various concentrations of NTA, all at pH 12.
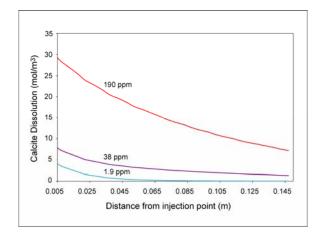

Figure 6. Simulated calcite dissolution vs. distance along the flow reactor after 1.5 days for solutions of varying NTA concentration. The pH was 12 and the flow rate was 1 ml/min.

Figure 7 illustrates the advantage of the chelating agent NTA over HCl for removing calcite scale within geothermal wellbores. It shows that similar volumes of scale are removed, but NTA allows for a more even dissolution of calcite along the entire length of the reactor. Similarly, and as discussed above, an NTA treatment within a scaled geothermal wellbore will allow for a more complete removal of calcite along the entire open-hole section.
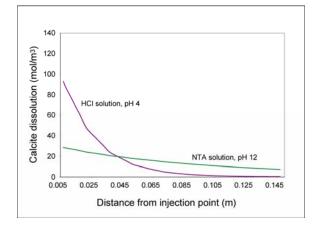

Figure 7. Simulation of calcite dissolution vs. distance along the flow reactor after 1.5 days for the mineral dissolution agents HCl and NTA.

Silica Dissolution

The silica dissolution rate expression is critical for the successful modeling of the silica dissolution process. The following expression is used in the present work (Xu et al., 2006):

$$r = A k_{25} \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]\left(1 - \frac{c}{K}\right) \quad (1)$$

where r is silica dissolution rate (moles per unit mineral surface area and per unit time, mol/m^2/s), A is the specific reactive surface area (m^2/g mineral), k_{25} is the rate constant at 25°C, E_a is the activation energy (kJ/mol), R is gas constant, T is absolute temperature, c is silica concentration, and K is silica mineral solubility.

Three parameters: A, k_{25}, and E_a, are needed using rate expression (1). Total amounts of silica dissolved during 2 hours of experiments for temperatures of 150, 200, 250 and 300°C, were measured in the laboratory experiments (see Figure 4). The parameters in the rate expression Eq. (1) can be obtained by calibrating measured data. We assumed reactive surface area $A = 1.31 \times 10^{-2}$ m^2/g because A and k_{25} are related by the product term in Eq. (1). Therefore, only k_{25} and E_a need to be calibrated. Four

simulations corresponding to four temperatures were performed. The simulated total amounts of silica are made to match measurements by adjusting values of k_{25} and E_a (trial and error method).

The resulting match (see Figure 8) was obtained using $k_{25} = 5.64 \times 10^{-8}$ mol/m^2/s and $E_a = 52.5$ kJ/mol. Variation of the amount of silica dissolved with temperature is reflected by the activation energy term E_a. The calibrated E_a value here for the silica glass is slightly smaller than E_a values of 60.9 – 64.9 kJ/mol reported by Rimstidt and Barnes (1980) for amorphous silica dissolution. The calibrated set of parameters reproduced measured amounts of silica well for temperatures ranging from 150 to 250°C, but not well for temperatures above 250°C. For the latter temperature range, a smaller E_a value may be required.
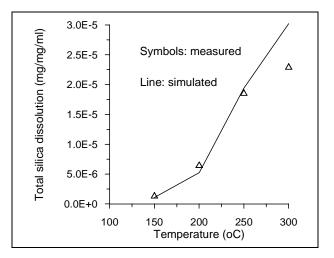

Figure 8. The simulated total amounts of silica dissolved together with measured data obtained using $k_{25} = 5.64 \times 10^{-8}$ mol/m^2/s and $E_a = 52.5$ kJ/mol.

With the calibrated set of parameters, we performed numerical experiments using a temperature of 250°C and a range of flow rates of 2.5, 5, 7.5 and 10 ml/min. The simulated silica concentration and silica dissolved per unit core volume along the flow path after two hours are presented in Figures 9 and 10, respectively. Silica concentrations increase linearly, indicating that silica dissolution is kinetically-controlled and the rates are nearly constant along the flow path. The largest slope is at the lowest flow rate (2.5 ml/min, Figure 9). Increases in flow rate result in only slight increases in silica dissolution (Figure 10) under experimental conditions because large flow rates result in lower residence times. The kinetic control of dissolution is apparent from the fact that at the lowest rate (2.5 ml/min), less silica per unit core volume is removed near the outlet, where aqueous silica concentrations are greater, than at the inlet. If dissolution occurred subject to local equilibrium,

silica dissolution should progress from the inlet to the outlet, with the advancement of the silica dissolution front proportional to total throughput of aqueous phase, i.e., proportional to flow rate.
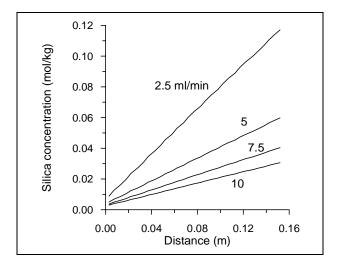

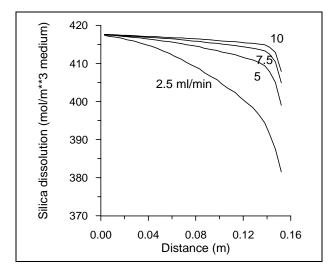*Figure 9. Simulated spatial distribution of silica concentration after two hours for different rates (at 250°C)*

Figure 10. Simulated cumulative silica dissolved after two hours for different flow rates (250°C)

SUMMARY AND CONCLUSIONS

A laboratory flow reactor was redesigned to avoid flow bypassing, and tracer tests were conducted which confirmed that flow occurs through the pore space along multiple pathways. Using a loading of glass beads as proxies for amorphous silica, silica dissolution experiments were carried out for temperatures from 150 - 300°C over time periods of two hours. TOUGHREACT simulations were able to match dissolution behavior for 150 - 250°C, using a kinetic rate expression from transition state theory,

and an activation energy close to previously reported experimental data. Numerical simulations were also performed to examine calcite dissolution behavior under alkaline conditions in the presence of chelating agents. Results suggest that this type of treatment may have distinct advantages over the current practice of using mineral acids for removing calcite scales, in that it effects a more gradual dissolution and thus should be capable of more uniform spatial coverage. A combined laboratory experimentation and modeling effort is underway to quantify and optimize scale removal by thermally stable chelates under alkaline conditions, and to design field trials of this novel technique.

REFERENCES

Fredd, C.N., Fogler, H.S. (1998) "The Influence of Chelating Agents on the Kinetics of Calcite Dissolution", *Journal of Colloid and Interface Science*, **204**, pp. 187-197.

Lund, K., Fogler, H.S., McCune, C.C., and Ault, J.W. (1975) "Acidization—II. The Dissolution of Calcite in Hydrochloric Acid", *Chemical Engineering Science*, **30**, pp.825-835.

Mella, M., Rose, P.E., Kovac, K., Xu, T., Pruess, K., and McCulloch, J. (2006) Calcite Dissolution in Geothermal Reservoirs Using Chelants, Geothermal Resources Council Transactions, San Diego, CA.

Rimstidt, J. D., and Barnes H. L. (1980) "The kinetics of silica-water reactions", *Geochim. Cosmochim. Acta,* 44, pp. 1683-1699.

Xu, T., Sonnenthal, E.L., Spycher, N., Pruess, K., (2006) "TOUGHREACT: A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media", *Computer & Geoscience*, 32(2), pp. 145–165.