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Numerical Simulation of Calcite Scale Removal by Chelating Agents Around a Geothermal Injection Well

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Geothermal injection well, chelating agents, calcite scale removal, porosity enhancement, reactive transport modeling

ABSTRACT
Geothermal injection wells are often drilled into formations containing calcite. Injecting chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA), could be effective for calcite dissolution and porosity enhancement around a geothermal well. This may overcome the problem that mineral acid (such as HCl) dissolves first-contacted minerals aggressively while leaving much of the rest of wellbore untreated. The reactive chemical transport modeling method is used to investigate the effectiveness of injecting chelating agents. The well configuration and data for hydrogeological conditions were taken from the Tiwi geothermal field, Philippines. Results indicate that calcite dissolution occurs significantly close to the injection well. The degree of the dissolution is gradually decreases along the flow path. Calcite dissolution increases accordingly the reservoir formation porosity, than the permeability could be significantly enhanced. Sensitivity regarding hydrological and chemical factors is discussed. Chelating agents could be potentially used for chemical stimulation of an EGS with calcite present.

1. Introduction
Geothermal injection wells are occasionally drilled into formations in which the fractures contain considerable amounts of calcite (Mella et al., 2006). Likewise, fluids within geothermal production wells often become oversaturated with calcium carbonate, resulting in calcite and/or aragonite deposition and the concomitant plugging of wellbores or near-wellbore formations. Scale-inhibition treatments through the continuous injection of scale-inhibitor chemicals via capillary tubing have been shown to prevent the deposition of calcite within wellbores, but such treatments have no effect on the near-wellbore formation. Removal of calcite from wellbores often is commonly accomplished by injecting strong mineral acid (such as HCl). Injected strong acid tends 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.

An alternative to the mineral acid treatment is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA). Mella et al. (2006) performed lab experiments using EDTA and NTA to investigate the effectiveness of chelating agents for calcite dissolution in the formation. A laboratory reactor was designed and fabricated for investigating calcite dissolution using these agents under controlled conditions that simulate a geothermal reservoir. Preliminary experimental data indicated that both EDTA and NTA are effective dissolution agents and that dissolution capacity increases with temperature.

Such 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, driving calcite dissolution. The kinetics of calcite dissolution using chelating agents is not as fast as is that using strong mineral acids. The lower dissolution rate makes the chelating agent take a more balanced path through the wellbore and more evenly dissolve calcite in all available fractures, rather than following the first fluid entry zone and leaving the rest relatively untouched.

The structures of the two chelating agents in anionic form are shown in Figure 1. In the calcite chelating process, one EDTA molecule will associate with two Ca²⁺ ions,

\[
\text{EDTA}^+ + 2\text{Ca}^{2+} = \text{Ca}_2\text{EDTA}
\]

(1)

allowing theoretically for the dissolution of two moles of calcite per one mole of EDTA. Two NTA molecules are required to dissolve three calcite molecules.

\[
2\text{NTA}^- + 3\text{Ca}^{2+} = \text{Ca}_3\text{NTA}_2
\]

(2)

Reactive chemical transport modeling is used here to study the effectiveness of injecting NTA chelating agent in field-like geothermal fractured conditions. A great deal of specific and detailed information is required to assess the chemical impact of an injection operation. The present study is not intended to represent any particular site. However, well configuration and
data for hydrogeological conditions were taken from hot brine injector Nag-67 in the Tiwi geothermal field, Philippines (Xu et al., 2004).

2. Numerical Modeling Approach

The present simulations were carried out using the non-isothermal reactive geochemical transport program TOUGHREACT, whose physical and chemical process capabilities and solution techniques have been discussed by Xu and Pruess (2001) and Xu et al. (2006). The simulator can be applied to one-, two-, or three-dimensional porous and fractured media with physical and chemical heterogeneity, and can accommodate any number of chemical species present in liquid, gas and solid phases. Temporal changes in porosity and permeability due to mineral dissolution and precipitation can modify fluid flow path characteristics. This feedback between flow and chemistry is considered in our model. Changes in porosity are calculated from changes in mineral volume fractions. Several porosity-permeability relationships are employed.

For the present work, the porosity-permeability relationship proposed by Verma and Pruess (1988), with a more sensitive coupling of permeability to porosity than the Kozeny-Carman relationship, was used:

\[
\frac{k}{k_0} = \left( \frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n
\]

In this equation, \( \phi_c \) is the value of “critical” porosity at which permeability goes to zero, and \( n \) is a power law exponent. Eq. (3) is derived from a pore-body-and-throat model in which permeability can reduce to zero with limit (“critical”) porosity remaining. Parameters \( \phi_c \) and \( n \) are medium-dependent.

3. Problem Setup

3.1. Flow Conditions

To explore effectiveness of chelating agents under field injection conditions, the well configuration and data for hydrogeological conditions were taken from hot brine injector Nag-67 in the Tiwi geothermal field, Philippines (Xu et al., 2004). A 120 m thick reservoir formation at the bottommost permeable zone of the injection well (Nag-67) was modeled. A simple one-dimensional radial flow model was used, consisting of 50 radial blocks with logarithmically increasing radii (Figure 1). The 50 blocks represent a distance of 1000 m from the wall of the drilled open hole. Only the fracture network is considered in the model, with the assumption that the fluid exchange with the surrounding low permeability matrix is insignificant. A fracture porosity of 1% (ratio of fracture volume over the total formation volume) was assumed. The initial bulk permeability has been estimated at \( 8.6 \times 10^{-14} \) m², to be consistent with the observed initial injectivity index of the well. The same volume of wall rock (1%) as fracture volume was considered, to allow mineral coated on the fracture interacting chemically with water. A total thickness of 2.4 fracture domain was modeled. Therefore, initial porosity of the modeled fracture domain is 0.5 and permeability is \( 120 \times 8.6 \times 10^{-14} / 2.4 = 4.3 \times 10^{-12} \) m². During the simulation, porosity is dynamically calculated from mineral dissolution and precipitation. Permeability is then calculated from porosity according to Eq. (3) with \( \phi_c \) value of 0.42 and \( n \) value of 3. Conductive heat exchange with rocks of low permeability above and below this zone is an important process. The confining layers are modeled as semi-infinite half spaces, and heat exchange is treated with a semi-analytical technique due to Vinsome and Westerveld (1980).

Initial reservoir temperature and pressure were assumed as 260°C and 20 MPa, respectively. Hydrogeologic specifications of the 1-D radial flow problem are given in Table 1. For a base-case simulation, an injection rate of 40 kg/s was applied for a period of 1 day. An injection temperature of 120°C was used. Injection water was assumed to have a NTA concentration of 5 mmol/kgw (w means \( \text{H}_2\text{O} \)), and a pH of 11. Concentrations of other chemical components are assumed to be very small.

<p>| Table 1. Geometric and hydrogeologic specifications for 1-D radial flow problem. |
|-----------------|------------------|------------------|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th><strong>Reservoir properties:</strong></th>
<th><strong>Permeability</strong></th>
<th><strong>Porosity</strong></th>
<th><strong>Rock grain density</strong></th>
<th><strong>Rock specific heat</strong></th>
<th><strong>Thermal conductivity</strong></th>
<th><strong>Initial and boundary conditions:</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>4.3x10^{-12} m²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pressure</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>200 bar</td>
</tr>
<tr>
<td>Rock grain density</td>
<td>2750 kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td>Rock specific heat</td>
<td>1000 J/kg°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>260 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>2.4 W/m°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td>200 bar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Temperature</td>
</tr>
<tr>
<td>Temperature</td>
<td>260 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2. Reaction Kinetics

It’s assumed that calcite and amorphous silica each have a volume fraction of 5%. The remaining 40% solid volume is considered as non-reactive. The calcite dissolution rate is five or six orders of magnitude faster than that of aluminosilicate minerals. The dissolution of calcite and amorphous silica is considered under kinetic constraints. A general form of rate expression is used, which is based on transition state theory (TST) (Lasaga et al., 1994):

\[
r = kA \left[ 1 - \left( \frac{Q}{K} \right) \right]^{\eta}\]

where \(r\) is the kinetic rate (units of moles per second; positive values indicate dissolution, and negative values precipitation), \(k\) is the rate constant (moles per unit mineral surface area and unit time) which is temperature dependent, \(A\) is the specific reactive surface area per kg H₂O, \(K\) is the equilibrium constant for the mineral-water reaction written for the destruction of one mole of mineral, and \(Q\) is the reaction quotient. The parameters \(\theta\) and \(\eta\) must be determined by experiment, but are commonly set equal to unity when experimental quantification is unavailable. The precipitation of secondary minerals is represented using the same kinetic expression as for dissolution.

For many minerals, the kinetic rate constant \(k\) can be summed from two mechanisms (Lasaga et al., 1994; Palandri and Kharaka, 2004):

\[
k = k^{25}_{\text{nu}} \exp \left[ \frac{-E^{25}_{\text{nu}}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] + k^{25}_{H} \exp \left[ \frac{-E^{25}_{H}}{R} \left( \frac{1}{T} - \frac{1}{298.15} \right) \right] a^{n_{H}}_{H}
\]

where subscripts nu and H indicate neutral and acid mechanisms, respectively, \(E\) is the activation energy, \(k^{25}\) is the rate constant at 25°C, \(R\) is the universal gas constant, \(T\) is absolute temperature, \(a\) is the activity of the species; and \(n\) is a power term (constant). Notice that parameters \(\theta\) and \(\eta\) (see Eq. 4) are assumed to be the same for each mechanism, and, for reasons noted above, are set to unity in the present work.

Mineral dissolution rates are a product of the kinetic-rate constant and reactive surface area as represented by Eq. 4. The parameters used for the kinetic rate expression are given in Table 2. We include separate rate constants \((k^{25})\), activation energies \((E)\), and reaction order \((n)\) for processes catalyzed by \(H^+\). At any pH, the total rate is the sum of the rates from the two mechanisms. Mineral reactive-surface areas (the third column of Table 2) are based on the work of Somnenthal et al. (2005), and were calculated assuming a cubic array of truncated spheres constituting the rock framework.

Aqueous reaction of Eq. (2), \(2\text{NTA}^3^- + 3\text{Ca}^{2+} = \text{Ca}_3\text{NTA}_2\), is also considered to proceed according to a kinetic rate. A simple linear kinetic rate expression for formation of \(\text{Ca}_3\text{NTA}_2\) or dissolution of Ca, is used here:

\[
r_{\text{Ca}} = k_{\text{Ca}} C_{\text{NTA}}
\]

where \(r_{\text{Ca}}\) is the rate (mol/s), \(k_{\text{Ca}}\) is rate constant (mol/kgw/s), \(C_{\text{NTA}}\) is NTA concentration (mol/kgw). In the current simulation, a \(k_{\text{Ca}}\) value of \(1.0 \times 10^{-2}\) mol/kgw/s was used, which was calibrated from the lab experiment of Mella et al (2006).

3.3. Simulations

Spatial distribution and temporal evolution of calcite dissolution around an injection well are sensitive to many hydrological and chemical factors. A total of three groups of (nine) simulations were performed. The first group was designed for studying effects of injection rate. Two additional injection rates of 20 and 60 kg/s, in addition to the base-case value of 40 kg/s, were used. The second group was intended for exploring effects of injection water temperature. Two additional values of 80 and 160 °C, in addition to the base-case of 120 °C, were used. In both group of simulations, the injection water chemistry remained the same as the base-case. The third group was for studying sensitivity of NTA concentration of injection water, using two values of 1 and 3 mmol/kgw, decreased from the base-case value of 5 mmol/kgw. The pH (11) was assumed to be the same as the base-case.

Many chemical factors could affect the performance of calcite dissolution and formation porosity enhancement, including calcite abundance and distribution in the formation, reaction kinetics of both calcite dissolution and chelation process. These factors will be investigated in the future with more data from laboratory experiments and field observations.

### Table 2. List of initial mineral volume fractions in and parameters for calculating kinetic rate constants of minerals.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Volume fraction in term of medium</th>
<th>Neutral mechanism</th>
<th>Acid mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (cm²/g)</td>
<td>k^{25} (mol/m²/s)</td>
<td>E (KJ/mol)</td>
</tr>
<tr>
<td>Calcite</td>
<td>5%</td>
<td>1.457×10⁻⁷</td>
<td>62.76</td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>5%</td>
<td>1.000×10⁻¹⁰</td>
<td>1.047×10⁻¹¹</td>
</tr>
<tr>
<td>Non-reactive minerals</td>
<td>40%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>50%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
r_{\text{Ca}} = k_{\text{Ca}} C_{\text{NTA}}
\]
the amount is several orders of magnitude smaller than calcite because of slow kinetics.

Variations in injection temperature affect slightly the calcite dissolution (Figure 3). The higher injection temperature causes slightly more calcite dissolution. Calcite dissolution is sensitive to NTA concentration in the injection water (Figure 4). A larger injected NTA concentration results in more calcite dissolution. Concentrations of NTA gradually decrease along the radial flow path (Figure 5).

5. Summary and Conclusions

Reactive chemical transport simulations have been performed using a 1-D radial model to study the effectiveness of calcite dissolution and porosity enhancement by injecting NTA chelating agent around a fractured geothermal injection well. Simulation results indicate that calcite dissolution occurs close to the injection well. The degree of the dissolution gradually decreases along the flow path. The reservoir formation porosity increases accordingly with calcite dissolution, and the permeability could be significantly enhanced. Calcite dissolution is sensitive to injection rate. More calcite dissolves at a higher injection rate, but the increase is less pronounced at higher injection rate. Variations in injection temperature affect the calcite dissolution only slightly. Calcite dissolution is sensitive to NTA concentration in the injection water, with larger NTA concentration resulting in more calcite dissolution. Chelate is an effective dissolution agent compared to mineral acid (such as HCl), which dissolves first-contacted minerals aggressively while leaving much of the rest untreated.

Many chemical factors could affect calcite dissolution and associated enhancement in formation porosity and permeability, including calcite abundance and distribution in the formation, reaction kinetics of both calcite dissolution and chelation process. These factors will be investigated in the future with more data from laboratory experiments and field observations. Chelating agents could be potentially used for chemical stimulation of an EGS with calcite present.
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