MODELING AMORPHOUS SILICA PRECIPITATION: A STRATEGY TO REDUCE SILICA PRECIPITATION NEAR COSO INJECTION WELLS

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ABSTRACT

To reduce long-term silica precipitation near injection wells, we evaluated three strategies to reduce silica precipitation: (1) “acid injection”, (2) “alternating acid and alkali injection”, and (3) injection through “multiple small diameter injection wells”. For each case, we modeled mineral precipitation from the injection point toward the production well. We found that “alternating acid and alkali injection” was the most effective strategy to reduce long-term silica precipitation near the injection point. (1) Acid injection reduces the kinetic rate of silica precipitation by reducing the pH. This strategy significantly reduces silica precipitation but the feedback effect of acid injection causes a more long-term precipitation problem. (2) Alternating acid and alkali injection reduces silica precipitation by alternating the fluid pH. The kinetic rate of silica precipitation is reduced when acid is injected. When alkali is injected, silica becomes undersaturated and dissolves by the formation of NaHSiO\textsubscript{3}(aq). Since the pH of mixed water is not modified by this treatment, no significant feedback effect is expected. (3) The use of small diameter injection wells and slow injection rate allows fast temperature increase down the well. The increased temperature results in higher solubility of silica and prevents silica precipitation near the injection point. This strategy, however, is limited by the slow injection rate and silica and calcite precipitation in the pipeline and wellbore.

INTRODUCTION

Produced geothermal water should be reinjected because of environmental concerns and long-term efficiency of power generation. Unfortunately, since the utilized geothermal water contains significant solute, the water precipitates minerals and will clog injection wells over time. Thus, it is important to address scaling problem for economical utilization of geothermal energy.

To exploit geothermal energy, geothermal brine is pumped from a hot reservoir and heat or steam is extracted from the brine. Because the hot brine is in equilibrium with rocks (Chan, 1989) it contains a large amount of dissolved solids. The geothermal water becomes oversaturated with many common minerals and precipitates them once the hot water is cooled by heat extraction or concentrated by the loss of steam. Thus, mineral precipitation is an inevitable problem in the exploitation of geothermal energy. Mineral precipitation occurs in many parts of the operation -- turbines, pipelines and injection wells, and cleaning is a costly operation (Henley, 1983).

The most common minerals precipitated from geothermal brine are calcite, sulfides and amorphous silica (Tassew, 2001). Among these scales, silica scaling is the biggest problem because it is hard and treatment is difficult once it precipitates. Due to the relatively slow dissolution rate of silica, it is not easy to remove silica scaling. In contrast, calcite and sulfide scaling are more readily dissolved and can be treated with acid. Minerals that precipitate near the injection well at Coso include amorphous silica and small amounts of calcite.

Many different approaches have been made to address silica scaling (Klein, 1995; Rothbaum et al., 1979; Sugita et al., 2000). One approach is to reduce the rate of silica scaling by reducing fluid pH (Rothbaum et al., 1979). This approach is theoretically sound and is a commonly recommended method. However, long-term consequences have not been addressed. The other approach is to reduce silica oversaturation with controlled silica precipitation. Sugita et al. (1998) actively precipitated silica to reduce silica oversaturation before reinjection. However, this approach produced large quantities of waste silica that had to be regularly removed and transported. Thus, we still do not have a suitable long-term strategy to reduce silica scaling.

To find an economic solution to reduce Coso silica scaling, we selected three strategies suitable for continuous operation and which would be maintenance free. We modeled the three strategies: (1) acid injection, (2) alternating acid and alkali injection, and (3) injection through multiple small diameter injection wells. We used X1t, a one-dimensional reactive transport model (Bethke, 2004).
SILICA SOLUBILITY

To control precipitation of amorphous silica, it is important to understand silica solubility. Solubilities of quartz and amorphous silica increase with increasing temperature (Figure 1). Since hot geothermal brine is commonly in equilibrium with quartz within the reservoir (Chan, 1989), silica concentration increases with increasing brine temperature. The solubilities of quartz and amorphous silica do not significantly depend on pH below pH 7 but they increase with increasing pH above 7 in brine containing sodium. The increased solubility is caused by the formation of sodium bisilicate at a high pH:

\[ \text{Na}^+ + \text{OH}^- + \text{SiO}_2(aq) \rightleftharpoons \text{NaHSiO}_3(aq) \]  

The reaction reduces the activity of SiO\(_2\)(aq) by producing NaHSiO\(_3\)(aq). The reduced SiO\(_2\)(aq) activity causes the dissolution of amorphous silica or quartz. Thus, increasing the pH can be a good strategy to reduce silica precipitation.

Another way to reduce silica supersaturation is to reduce the silica concentration. The silica-supersaturated injection water (A) can be diluted with shallow groundwater (B) at 15°C (Figure 1). Since the injection water (A) is above the solubility curve of amorphous silica, the mixed water can precipitate amorphous silica. To prevent silica precipitation, the injection water (A) should be mixed with groundwater (B) to produce mixed water (C) that plots slightly below the amorphous silica line. However, each volume of injection water requires about 2 volumes of groundwater resulting in a mixed water temperature of 50°C. This is not practical because of the shortage of groundwater and the mixed water will more rapidly cool the reservoir than will fluid A. Thus, we did not favor this strategy to reduce silica precipitation.

THREE STRATEGIES

We tested three strategies to reduce the silica precipitation. Although we will discuss all aspects of silica and calcite precipitation along the pipeline, well bore, and reservoir rock near the injection point, our primary objective is to reduce silica precipitation in the reservoir rock near the injection point. Once silica precipitation fills the pore spaces, the injection rate is irreversibly reduced, and the process can render the injection well useless. In particular, silica precipitation near the injection point can dramatically reduce the injection rate. If the silica precipitates further away from the injection point, the reduction in the injection rate will not be as significant. Thus, our strategy should be either: (1) to prevent silica precipitation near the injection point; or (2) to precipitate silica far away from injection point.

The first strategy, “acid injection” is commonly suggested as a way to reduce silica precipitation (Klein, 1995). By reducing the pH, the kinetic rate of silica polymerization is reduced and, therefore, silica precipitation is reduced.

The second strategy, “alternating injection of acid and alkali” is a strategy to undersaturate amorphous silica by increasing the pH. When alkali is injected, silica becomes undersaturated and dissolves rather than precipitates. This strategy sounds promising because we can even dissolve amorphous silica. However, a high pH causes precipitation of calcite and sulfide minerals. Furthermore, the injected high pH brine will dissolve more silica in the hot reservoir and, when the injected brine reaches the production well, can cause a more serious scaling problem. To prevent this feedback effect, we should not change the average pH of the injected water. This can be achieved by alternately injecting acid and alkali. Acid injection reduces the silica precipitation kinetic rate thus reducing silica precipitation, and acid will dissolve calcite and sulfide minerals. Alkali fluid will dissolve the precipitated silica, and perhaps deposit calcite and sulfide minerals. Hydrodynamic dispersion in the hot reservoir will mix the low and high pH waters away from the injection point resulting in a relatively neutral pH. Silica is thus expected to precipitate away from the injection point.

The third strategy is to use multiple small diameter injection wells (Sanyal et al., 2005). This approach
preheats the injected brine in the injection wellbore by using small diameter wells (2.5 to 7.5 cm) and slow injection rates (less than 10 liter/sec). When the brine reaches the injection point, the temperature of the brine is hot enough to prevent silica precipitation, thus preserving the permeability of the reservoir rock near the injection point. As the temperature of the brine is expected to increase away from the injection point, the brine becomes increasingly undersaturated preventing silica precipitation further away from the injection point.

These three strategies will be compared with the “untreated” case.

**REACTIVE TRANSPORT MODEL SETUP**

Figure 2 shows the simplified Coso geothermal power plant used for our simulation. Hot brine is extracted at the production well and steam is separated and the remaining brine is transported through the pipeline and reinjected at the injection well. The distance between the production and injection well is assumed to be 2 km and so is the length of the pipeline. We modeled mineral precipitation in the pipeline, injection wellbore, and reservoir rock from the injection point to 1 km away from that point. Since these three intervals are distinctly different, we created three different models, respectively for each interval. We assumed that acid and alkali is injected at the beginning of the pipeline (Figure 2).

Table 1 shows the chemical composition of the water injected into well 68-20. Although other major and trace chemical components are present, we did not incorporated them into the model because only amorphous silica and calcite were observed as mineral scales around the injection well (McLin et al., 2006) and other chemical components do not significantly affect the saturation of these minerals. Chloride has little effect on mineral saturation but it was included for charge balance considerations and B(OH)$_3$ is included because of its buffering capacity, which affects the pH when acid or alkali is injected.

Table 1. Chemical composition of initial and inlet water used for the modeling. This chemistry is chosen considering the chemistry of injected Coso water (Coso 68-20).

<table>
<thead>
<tr>
<th>Inlet and initial water</th>
<th>Temp (°C)</th>
<th>pH</th>
<th>B(OH)$_3$</th>
<th>Ca$^{2+}$</th>
<th>Cl$^-$</th>
<th>HCO$_3^-$</th>
<th>Na$^+$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>105</td>
<td>7</td>
<td>10 mM</td>
<td>1 mM</td>
<td>200 mM</td>
<td>2.8 mM</td>
<td>200 mM</td>
<td>11 mM</td>
</tr>
</tbody>
</table>

B(OH)$_3$ is expected to buffer the pH with the following reaction:

$$
\text{BO}_2^- + \text{H}_2\text{O} + \text{H}^+ \rightleftharpoons \text{B(OH)}_3(\text{aq})
$$

(2)

Another pH buffering reaction is the bicarbonate buffer:

$$
\text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}
$$

(3)

The pipeline and wellbore are simulated with the simple 1-D reactive transport model shown in Figure 3. At the left boundary, flow velocities are set to 50 cm/sec in the pipeline and 100 cm/sec in the wellbore. The diffusion coefficient is set to $1\times10^{-8}$ cm$^2$/sec and longitudinal dispersivity to 1 cm. For the pipeline model, the temperature at the injection point is set to 130 °C and allowed to decrease linearly to 105 °C to simulate heat loss (Figure 4a). In the case of the wellbore model, the temperature is assumed to be constant at 105 °C except for the
“small diameter” case in which temperature increases linearly from 105 °C to 145 °C (Figure 4d).

Figure 4. Temperatures of (a) pipeline water from the flash plant; (b) water from the injection point for the case of acid or acid/alkali injection; (c) water from the injection point for the case of the small diameter wells; and (d) water in the wellbore for the case of the small diameter wells.

To simulate radial flow of the injected brine through the reservoir rock from the injection point, we created a radial flow model (Figure 5). The inner radius of the model is 12 cm, which is the radius of the injection screen and the outer radius is 1000 m, which is about the half of the distance between the production and injection wells. The porosity is set to 0.2. At the injection point, the flow velocity is 5 cm/sec and the velocity decreases away from the injection point. When brine exits at the right side of the model, the velocity is about 0.0006 cm/sec. Longitudinal dispersivity is set to 10 cm. X1t cannot simulate heat flux. Thus, we set the model temperature with an assumption of constant heat flux from the bottom. At the injection point, the temperature is set to 105 °C and the temperature increases quadratically to 185 °C (Figure 4b). For the case of the small diameter wells, the temperature at the injection point is 145 °C and increases quadratically to 225 °C (Figure 4c).

We assumed that silica is initially present in small quantities (10⁻⁵ volume %) to provide an initial surface to grow on and we did not consider homogeneous silica nucleation. Although other silica minerals such as quartz, or chalcedony are expected to precipitate, we did not consider these minerals because of their slow kinetic rate at our temperature of interest (105 °C) and because they were not found in Coso samples studied by McLin et al., (2006).

We assumed that the kinetic dissolution rate constant is the same as the precipitation rate constant. The rate constant \( k_+ \) (mol/cm²/sec) of silica dissolution at 100 °C is 10⁻⁸.⁶ (Icenhower and Dove, 2000) and the

Figure 5. Radial flow model from the injection point.

Figure 6. Kinetic rate constant \( k_+ \) of amorphous silica (Iler, 1979). The solid line is the fitted line used for the modeling. Squares represent data points.
kinetic rate (mol/sec) of silica dissolution and precipitation is given as:

\[ \text{rate} = k_+ A (1 - \frac{Q}{K}) \]  

(4)

where A is surface area given in cm\(^2\), Q is activity product, and K is equilibrium constant. We used the rates of silica dissolution as a function of pH by Iler (1979). Figure 6 shows the kinetic rate constant of amorphous silica as a function of pH at 100 °C. The kinetic rate of calcite is several orders of magnitude higher than that of silica (Sjoeberg and Rickard, 1984). Thus, we assumed that calcite precipitates or dissolves instantly reaching equilibrium with the brine.

Figure 7. The pattern of mineral precipitation and dissolution when (a) acid or (b) alkali is injected.

**MODELED RESULTS**

The pH controls the precipitation and dissolution of amorphous silica and calcite (Figure 7). When acid is injected (Figure 7a), the pH is low and calcite dissolves because it is undersaturated. However, silica is supersaturated and slowly precipitates in the pipeline, wellbore and reservoir rock near injection point. When alkali is injected (Figure 7b), the pH becomes high and high pH prevents precipitation of amorphous silica. In contrast, calcite becomes supersaturated and precipitates in the pipeline. Since calcite precipitation is a very fast process, calcite precipitates at the beginning of the pipeline. It does not precipitate away from the injection point because of the decrease in temperature along the pipeline, which results in the undersaturation of calcite.

Consequently, calcite will be undersaturated in the wellbore reservoir rock near the injection point.

Figure 8. pH of pore fluid from the injection point to the production well after 190 days. (a) “untreated” case, (b) “acid injection” case, (c) “alternating acid and alkali injection” case, and (d) “small diameter wells” case.

When the brine is “untreated”, the pH of the pore water near the injection point is about 7. It decreases slightly away from the injection point (Figure 8a). Calcite is undersaturated near the injection point and amorphous silica is slightly oversaturated but it becomes undersaturated away from the injection point due to the increase in temperature (Figure 9a). Relatively large amounts of amorphous silica precipitate near the injection point, which will cause clogging of the injection well (Figure 10a). Calcite precipitates away from the injection point due to the increase in temperature. Along the pipeline and wellbore, calcite precipitates at the beginning of the pipeline and silica precipitates everywhere. The rate of silica precipitation is about 50 times faster than that of other treated cases. Because silica precipitates
near the injection point, silica scaling can be very effective in clogging (Figure 10a).

When we injected “acid”, the pH of the water near the injection point is close to 3. The low pH water advances about 400 m after 190 days (Figure 8b). Due to the low pH, calcite is undersaturated near the injection point but the degree of amorphous silica oversaturation is greater near the injection point compared to the “untreated case” (Figure 9b). The low pH reduces the kinetic rate of silica precipitation. Thus, a relatively small amount of amorphous silica precipitates near the injection point (Figure 10b). Calcite precipitates far away from the injection point. The low pH also prevents calcite precipitation in the pipeline and wellbore. Therefore, this strategy will not result in calcite precipitation in pipeline, wellbore, and reservoir rock near the injection point. However, slow silica precipitation is expected everywhere.

For the “alternating acid and alkali injection” case, we inject acid for 20 days and then inject alkali for 20 days. Thus, the pH at the injection point changes over time (Figure 11a-c). The lowest pH is about 2.26 and the highest pH is about 8.44. Due to the different buffering behavior of the fluid with respect to acid and alkali, the pattern of pH change is not symmetrical. As shown in Figure 11c, the injected acid and alkali mixes away from the injection point. The pH of the mixed solution reaches about pH 7 after 190 days (Figure 8c). The saturation indices of amorphous silica and calcite change as a function of pH. At a high pH, amorphous silica is undersaturated and calcite is oversaturated. The reverse relationships are found at a low pH (Figure 9c). After 190 days, a
small amount of amorphous silica and calcite have precipitated (Figure 10c). The amount is comparable to that of the “acid injection” case. Calcite precipitates near the injection point. However, since the kinetic rate of calcite is very fast, the next “acid injection” will completely remove the calcite precipitation. Silica and calcite did not accumulate along the pipeline and wellbore.

The pH of the water near the injection point for the case of “multiple small diameter injection wells” is about 7 and changes little away from the injection point (Figure 8d). Near the injection point, amorphous silica is slightly oversaturated and calcite is undersaturated (Figure 9d). Little amorphous silica precipitates near the injection point and calcite precipitates away from the injection point due to the increase in temperature (Figure 10d). Although this strategy completely eliminates silica precipitation near the injection point, silica and calcite precipitate rapidly along the pipeline and wellbore due to high rate of silica precipitation and temperature increase along the wellbore.

DISCUSSION

Compared with the “untreated” case, all three strategies significantly reduced silica precipitation near the injection point. The first strategy, “acid injection” reduced silica and calcite. As shown in Figure 10b, this method results in the least amount of silica scaling near the injection point. Compared with the second strategy, however, silica scaling starts closer to the injection point, and is potentially more likely to clog of injection wells. The largest problem with this strategy is the “feedback effect” of acid injection. Since this method injects “acid”, the low pH will significantly increase dissolution of silicate, carbonate, and sulfide minerals in the hot reservoir. Thus, a high solute concentration may occur at the production well unless it is mitigated by dilution with low salinity reservoir waters. Due to this feedback effect, “acid injection” may not be a good long-term strategy.

The second strategy, “alternating injection of acid and alkali” is effective in reducing silica scaling. In fact, silica scaling was completely prevented within 50 m from the injection point. Thus, this strategy will be very effective to prevent clogging of the reservoir rock around the injection wells. However, it is more complex and will cost more to operate than “acid injection” because a large amount of acid and alkali should be injected. Since injected acid and alkali are mixed and become neutral, acid and alkali injection may not significantly modify solute concentration at the production well over time.

The third strategy “multiple small diameter injection wells” was effective in removing silica precipitation near the injection point. However, this strategy did not address silica and calcite precipitation along the pipeline and wellbore. Therefore, this method should be used with other means to remove mineral precipitation in the pipeline and wellbore. Furthermore, the slow injection rate required for this method may limit the application of this method.

REFERENCES


