Laboratory Experiments on Prevention and Dissolution of Silica Deposits in a Porous Column (1): Solid Deposition Due to Silica Particle Aggregation and Inhibition by Acid Dosing

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ABSTRACT
Solid deposition in geothermal reinjection brines, the primary mechanism of which is the aggregation of silica particles, has been investigated in the laboratory at the Kakkonda geothermal power plant. Experiments show that fluid temperature does not influence silica particle aggregation, while sulfuric acid dosing affects particle dispersion, as well as silica polymerization rates. These results will contribute to improve energy utilization in geothermal power plants.

Introduction
The deposition of silica in reinjection brines limits the amount of geothermal heat that is available for power generation. Further cooling of the brine in the heat exchangers of a bottoming binary cycle, or the decrease of the flashing temperature in a flash cycle may induce additional silica scaling.

At the Kakkonda geothermal power plant, Tohoku District, Japan, a feasibility study is being done on the introduction of a binary power plant that would use reinjection water as the heat source. Laboratory experiments investigating silica deposition were performed to study the effects of increasing the amount of heat recovered from reinjection brines. The objectives of this work are: (1) to investigate silica scaling behavior when reinjection brine temperature is decreased; (2) to evaluate the effects of sulfuric acid dosing on silica scaling; and (3) to develop a method to dissolve silica scale by alkali dosing.

The focus of these experiments is to study particle aggregation as the primary mechanism of solid deposition, a phenomenon that has not been investigated adequately. This paper mainly presents the influence of lowering the brine temperature on particle aggregation and the effects of acid dosing the reinjection brine to prevent silica scaling.

Laboratory Experiments
Solid deposition from reinjection brine was investigated in the laboratory in 2011. Brine from Well pad No. 5 at the Kakkonda geothermal field was used. Three sets of experiments were performed; i.e., without chemical dosing (Run 1), with acid dosing (Run 2), and with alkali dosing (Run 3). In Runs 1 and 2, the effects on deposition of different reinjection brine temperatures were compared using two experimental apparatus setups. One is for high-temperature reinjection brine (Line 1), and the other for low-temperature reinjection brine (Line 2).

Experimental conditions are given in Table 1. The sulfuric acid dosing rate in Run 2 was kept constant; while sodium hydroxide was dosed intermittently in Run 3. Prevention and dissolution of solids deposits in Run 3 were presented by Fukuda et al. (2012, this volume). During each run, the chemistry of the reinjection water was kept nearly unchanged; the typical composition is given in Table 2.

Table 1. Experimental conditions.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature [°C]</th>
<th>Flow rate [L/min]</th>
<th>Dosing Reagent</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1 Line 1</td>
<td>120</td>
<td>1.33</td>
<td>-</td>
<td>8.1</td>
</tr>
<tr>
<td>Line 2</td>
<td>95</td>
<td>1.33</td>
<td>-</td>
<td>8.1</td>
</tr>
<tr>
<td>Run 2 Line 1</td>
<td>120</td>
<td>1.33</td>
<td>Sulfuric acid</td>
<td>4.9</td>
</tr>
<tr>
<td>Line 2</td>
<td>95</td>
<td>1.33</td>
<td>Sulfuric acid</td>
<td>4.9</td>
</tr>
<tr>
<td>Run 3 -</td>
<td>95</td>
<td>1.33</td>
<td>Sodium hydroxide</td>
<td>Various</td>
</tr>
</tbody>
</table>

Table 2. Typical chemical composition of the test fluid.
<table>
<thead>
<tr>
<th>Item</th>
<th>Value [-]</th>
<th>Concentration [mg/L]</th>
<th>Concentration [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH at Room Temperature</td>
<td>8.1</td>
<td>Na 666</td>
<td>K 74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca 23.3</td>
<td>Mg 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al 0.42</td>
<td>Fe 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl 1030</td>
<td>SO4 114</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B 28.3</td>
<td>SiO2 436</td>
</tr>
</tbody>
</table>
A schematic of the experimental apparatus is shown in Fig. 1. Wet parts of the instruments and equipments are made of stainless steel or PTFE to avoid corrosion. The basic design is similar to the apparatus described by Mroczek et al. (2000) and Mejorada et al. (2000). It consists of four major components, namely a chemical dosing part, a heat exchanger, storage tanks, and a porous column. Reinjection brine is branched from the main reinjection brine line at the pad and sent to the apparatus. During each run, the fluid flow rate in the apparatus is kept constant (i.e., 1.33 L/min) using the feedback control of the line pump speed.

Chemicals are injected into the test fluid using a metering dosing pump. The test fluid and the chemicals are mixed using a line-mixer. Downstream of the mixer, the test fluid is divided into Lines 1 and 2 and sent to the heat exchangers. The chemical concentrations in the test fluid was constant as the fluid flow rates and the chemicals were kept stable during each run.

Each line was fitted with a heat exchanger to lower the test fluid temperature. However, the heat exchanger in Line 1 was not operated during Runs 1 and 2. The original reinjection brine temperature was about 130°C. The temperature of test fluid was decreased to about 120°C in Line 1, and to about 95°C in Line 2.

The cooled fluid was pressurized and sent to two storage tanks whose purpose was to simulate silica polymer growth (or dissolution), and particle aggregation (or dispersion) during the period that the reinjection water travels from the chemical dosing point to the reservoir. The volume of these tanks was designed so that the total storage time was about an hour. The properties of the test fluid during storage were monitored by sampling and analyzing the fluid using a number of valves in the storage tanks. Subsequently, the test fluid was sent to a porous column, where the deposition of solid in the reservoir around a reinjection well is simulated.

The porous column is in a 25 mm diameter tube packed with 2 mm diameter zirconia beads. Pressure loss in the porous column is expected to increase due to the deposition of solids on the beads, which was monitored by measuring the differential pressure between the inlet and the 12 pressure measuring ports installed along the tube. The zirconia beads in 12 cells, which are separated by stainless steel meshes, were sampled separately after the test. The test fluid in the porous column was depressurized and separated by stainless steel meshes, were sampled separately after the test fluid was sent to a porous column, where the deposition of solid in the reservoir around a reinjection well is simulated.

The differential pressure between the porous column inlet and each of the pressure ports were measured once a day, which represents the solid deposition rate relevant to reservoir blockage. The permeability of the porous column was calculated using Darcy’s law:

$$Q = \frac{k \Delta P}{\mu L}$$  

(1)

where, \(Q\) is the volumetric flow rate (m³/s), \(k\) is the permeability (m²), \(A\) is the cross sectional area (m²), \(\Delta P\) is the differential pressure (Pa), \(\mu\) is the dynamic viscosity (Pa•s), and \(L\) is the length of the porous column between the reference point and a specified location (m).

After the test, the zirconia beads in each cell of the porous column were sampled and weighted. The solids on the beads were analyzed by X-ray diffraction (XRD) and scanning electron microscope and energy dispersive X-ray analysis (SEM-EDX).

**Results and Discussion**

The mass of the deposited solids normalized by the mass of a bead is shown in Fig. 2. In Run 2 more than 90% of the silica scaling was inhibited, when compared to Run 1. Considering measurement errors, almost no solid was deposited on the beads in Run 2. Therefore, we will focus on the deposition during Run 1.

The EDX analysis revealed that the deposits were composed mainly of Si, Al and O, for both temperatures. The XRD analysis indicated that the deposits were identified as the silica scale deposits found in Kakkonda.

![Figure 2. Mass deposited in the porous column after the 20 day experiments, where, Run 1: without chemical dosing, Run 2: with sulfuric acid dosing, Line 1: 120°C, Line 2: 90°C.](image-url)

The average mass of the deposits was 0.0024 g/g in Line 1, and 0.0023 g/g in Line 2. Within the measurement errors, there is no significant difference between the results corresponding to 120° and 95°C. The mass decreases along the length of the column i.e., it was higher at the column inlet. This trend was especially obvious in Line 2.

Shown in Fig. 3 is a typical photograph of the solid deposits on the beads near the...
inlet in Line 1. The deposits seemed to consist mainly of particles and their aggregates; the amount decreased with distance from the column inlet.

Typical pictures of solid deposits in Line 2 observed by SEM are shown in Figs. 4 and 5, where two types of deposits were detected. One was a film-like deposit and the other was an aggregate of particles. The thickness of the film-like deposits was observed to be about 2 μm consistently on all beads, regardless of reinjection brine temperature and location along the column. In general, there was a distribution in the size of the deposited particles, ranging from several tens of nanometer to ten micrometer. A regularity of particle or aggregate size due to a difference in location and test fluid temperature was not observed.

The mass of film-like deposits is about 0.002 g/g, which was estimated by considering that their thickness was 2 μm. This value corresponds to the mass of deposits near the outlet. The dissimilar mass deposited mass around the inlet and outlet of the column are attributed to a differences in the amount of particle aggregates. This agrees with the observed distribution of particle aggregates.

Figure 6 shows the changes in permeability in the porous column from the inlet to each of the measuring ports versus time. The “0-15 plot” corresponds to the first 15 mm section of the column; it represent the permeability around the inlet, while the plot of “0-715 plot” corresponds to the 715 mm long section; it represents the average permeability of the entire porous column.

At any point within the column the permeability decreases with time. Notice that the permeability is reduced more rapidly near the inlet than along the entire column. It is considered that this decline is mainly caused by particle aggregates on the beads because (1) these aggregates were observed to be deposited mainly near the inlet, and (2) the permeability is little affected by the film-like deposits.

Next, we will discuss the origin of the particle aggregates. The silica concentration, 436 mg/l in Table 2, indicates that the reinjection brine is undersaturated at 120 °C, and supersaturated at 95 °C, with respect to amorphous silica. Figure 7 presents the concentrations of monomeric and total silica in the brine collected from the five sampling valves (SVs), for the both temperatures. The figure shows the change in concentration with time in the direction of SV-A to SV-E, for a retention time of an hour. The concentrations of monomeric silica and total silica were constant for this retention time, within analytical errors. This implies no significant polymerization of dissolved silica occurred in the column even at 95°C, when the brine was supersaturated with respect to amorphous silica.

Assuming that the size or numbers of particles increase due to silica polymerization, it is expected that the amount of solid deposits would be larger for low temperatures as under these conditions, the rate of silica polymerization increases with decreasing brine temperature conditions. This agrees with the results of Weres et al. (1980). In Run 1, however, there is no significant difference between the results for 120° and 95°C, implying that the particles that existed in the test fluid have not grown by silica polymerization after test fluid was cooled. In addition, it shows that the film-like deposits are not caused by silica polymerization and that the origin of
these deposits is also related to the small particles that existed in the initial test fluid, and that the amount of film-like deposit was constant regardless of fluid temperature.

Based on the above, it is concluded that the primary mechanism of solid deposition was aggregation of silica particles, a mechanism not affected by fluid temperature.

In Run 2, most of deposits are inhibited by acid dosing, which generally lowered the rate of silica deposition due to a decrease in silica polymerization rate. In this experiment, however, the rate of solid deposition dropped, although the deposition was caused by the aggregation of silica particles. This implies that acid dosing, especially with sulfuric acid dosing, affects particle dispersion, as well as silica polymerization rate.

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Conclusions

Solid deposition from reinjection brine, in which no significant silica polymerization occurs, has been investigated in laboratory experiments. The solids deposit due to the aggregation of particles in despite of the limited progress of silica polymerization reactions. The results of the experiments indicate that fluid temperature does not affect the amount of solid deposition. It is concluded that fluid temperature has no effect on solid deposition under the assumption that the primary mechanism is aggregation of silica particles.

Most silica deposition is inhibited by sulfuric acid dosing. The experiments show that this dosing decreases silica deposition although no significant silica polymerization occurs without this treatment. This implies that acid dosing, especially sulfuric acid dosing, affects particle dispersion, as well as silica polymerization rate.

This work shows that particle aggregation may be a significant mechanism in silica deposition from geothermal reinjection brine. Further work is required to understand the particle aggregation mechanisms, and develop methods to disperse particles, which will help improve energy utilization in geothermal power plants.

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References

