Silica scaling: The main obstacle in efficient use of high-temperature geothermal fluids

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Abstract

Utilization of geothermal resources involves cooling of the geothermal fluid by extraction of heat from it. In the case of high-temperature geothermal fluids, precipitation of amorphous silica from solution to form silica scales is the main obstacle for efficient heat extraction. The silica scale formation causes operational problems and may even clog pipelines and injection drill holes. The rate of silica scale formation can be reduced by aging amorphous silica over-saturated waters, which allows the aqueous silica in excess of saturation to polymerize. Polymeric silica has lesser tendency to precipitate from solution than monomeric silica. Studies of separated water from the Nesjavellir geothermal power station, Iceland, indicate that silica scale formation can be avoided during heat extraction by rapid cooling in "capillary heat exchangers". Scale formation from the amorphous silica over-saturated water leaving the heat exchanger, which is to be injected, can then be eliminated by aging the water for one to two hours and subsequently mixing it with condensed steam.

Keywords: silica, polymerization, scaling, injection.

1 Introduction

Heat extraction from high-temperature geothermal waters is usually restricted by troublesome silica scale formation as the water cools down. Reduction or even elimination of silica scale formation by appropriate handling of the water would open up opportunities for increased efficiency in the use of high-temperature geothermal resources.

Silica concentrations in 200-350°C aquifer waters of geothermal systems are about 300-700 mg/kg SiO₂ and they are controlled by quartz solubility (Fournier and Rowe, 1966; Mahon, 1966). The temperature of the flashed reservoir water at the wellhead is usually between 160° and 250°C depending on the wellhead pressure. Further cooling may occur by conduction at the surface, particularly if the water is passed through heat exchangers. Silica minerals possess prograde solubility and during cooling, usually between 100° and 200°C, saturation is reached with respect to amorphous silica. Its precipitation rate is fast resulting in potential deposition of this phase if the water is cooled below its saturation point. To avoid amorphous silica scaling it is common to dispose of spent high-temperature water at temperatures above amorphous silica saturation, e.g. by injection into wells. This method of disposal involves inefficient use of the heat energy brought to the surface. Experience at Nesjavellir, Iceland, indicates that efficient heat extraction from the separated water is possible without producing silica scales. By using heat exchangers consisting of pipes with a small diameter, and correspondingly thin walls, the separated water can be cooled by passing it through them in a matter of seconds. Such short residence time, experience indicates, is not sufficient for onset of silica deposition. This method of extracting heat from the wastewater does not solve the problem of disposal by injection. Injection of amorphous silica over-saturated water from the heat exchangers

may be difficult as silica deposition rate is sufficiently rapid to cause operational difficulties, even clog injection wells and the receiving aquifer.

Two kinds of processes involving aqueous silica tend to occur in an amorphous silica over-saturated solution. Firstly, there is a tendency for the water to precipitate amorphous silica directly onto a surface. Secondly, the silica tends to polymerize and form colloids that may remain suspended in the solution for long periods of time. Polymeric silica has lesser tendency to precipitate from the solution than monomeric silica. The relative rates of the two reactions, amorphous silica deposition and silica polymerization and the rate, by which polymeric silica settles from solution, determine how successful polymerization treatment is in reducing silica deposition from geothermal wastewaters. In the Otake geothermal area, Japan, this type of treatment reduced silica deposition in the pipelines by a factor of 10 (Yanagase et al., 1970).

Knowledge of the kinetics of silica polymerization is very important, as it determines how long the geothermal waters has to be aged to reduce the rate of amorphous silica deposition to an acceptable level. This paper presents some experimental work on the kinetics of silica polymerization, both on synthetic silica solutions and geothermal water from the Nesjavellir power plant, Iceland. In conjunction with these experiments a pilot plant was built at the power plant to test the aging processes of the geothermal waters (Gunnarsson et al. 2002).

2 Kinetics of silica polymerization

The kinetics of silica polymerization depends of several factors, such as solution pH, ionic strength, temperature and amorphous silica over-saturation (Chan, 1989; Weres et al., 1981; Rothbaum and Rohde, 1979; Iler, 1979). These are the same factors that control rates of amorphous silica deposition. Increased rate of silica polymerization therefore implies increased risk of silica scaling.

In geothermal waters, the factors determining the rates of silica deposition and polymerization can be controlled to some extent by adding an acid or a base to the water to adjust the pH-value or by adding salt to increase the ionic strength and therefore enhancing polymerization rate. Such treatment involves considerable cost because the amount of wastewater from geothermal plants can be more than 5 l/s per produced MW, and may therefore not be acceptable economically. Temperature and over-saturation are factors that are very much related when dealing with specific geothermal water. These factors can easily be controlled with little cost and their effects on polymerization rates will be studied in this paper.



Figure 1: Effects of over-saturation on the rate of silica polymerization. The dotted line represents amorphous silica solubility at 83°C.

Experiments were performed in 500 ml polypropylene bottles in a temperature controlled water bath. The salinity of the solutions was kept at minimum and was close to 0.01M in all cases. The pH-values of the solution measured at room temperature were between 8 and 9. Synthetic solutions were prepared by dissolving silica gel in a 0.1 N NaOH solution and subsequently diluted with de-ionized water to obtain the desired silica concentration. Decreasing the pH-value by the use of concentrated HCl triggered silica polymerization. The molybdosilicic method was used to measure Monomeric silica concentration.

2.1 Effects of amorphous silica over-saturation on silica polymerization

Figure 2 shows results from three experiments performed at 83°C but with different initial levels of amorphous silica over-saturation. The degree of over-saturation has strong effects on silica polymerization rates. The silica concentration in a solution, which initially contained 777 mg/kg unionized monomeric silica (as SiO₂), decreased to around 400 mg/kg in 50 minutes. During the same period of time the monomeric silica concentration of a solution initially containing 638 mg/kg SiO₂ only decreased to 616 mg/kg and the monomeric silica concentration of a solution that initially contained 458 mg/kg SiO₂ decreased even less. The induction period becomes longer with decreased degree of over-saturation. The relatively long induction period can be explained by the high solubility of the initially formed polymers and the fact that dimers and trimers break down fast enough to react with the molybdic acid, to form the yellow molybdosilicic complex.



Figure 2: The effect of temperature on kinetics of silica polymerization. The dotted lines represent amorphous silica solubility at 60° and 83°C, respectively.

2.2 Effects of temperature on silica polymerization

The rate of silica polymerization in a solution containing around 700 mg/kg unionized monomeric silica (as SiO₂) is faster at 60°C than at 83°C (Fig.2). The rates of chemical reactions generally increase with rising temperature. Over-saturation with respect to amorphous silica is higher in the 60°C solution, or 440 mg/kg compared to 403 mg/kg in the 83°C solution (Fig. 2). The higher degree of over-saturation apparently is sufficient to outweigh the effect of increase in temperature from 60° to 83°C on the rate of silica polymerization.

3 Changes in pH-value and mineral saturation

Silica polymerization lowers the aqueous concentration of monomeric silica significantly, reducing potential amorphous silica deposition as well as the potential precipitation of any silica-bearing mineral.

After flashing, high-temperature geothermal waters in Iceland usually have a pH-value between 8-10 and are buffered by monomeric silica, which forms a weak acid in water with a logK value of -9.9 at 25°C. During polymerization unionized monomeric silicic acid is removed from the solution causing an increase in solution pH. This does not apply for waters with lower pH-values buffered by other weak acids. Changes in pH during silica polymerisation are shown in Figure 3, both as bases on direct measurement of the pH (at room temperature) during polymerization as well as calculated pH change using the WATCH speciation program (Arnórsson et al., 1982) version 2A (Bjarnason, 1994). These values are in quite good agreement. The difference may not be significant. However, the observed difference could be caused by the presence of dimeric, trimeric and polymeric silica which forms stronger acid in solution than monomeric silica (Iler, 1979) releasing protons back into solution decreasing the pH-change. The WATCH program does not take into account the presence of the polymeric silica species.



Figure 3: Changes in pH during silica polymerization. The open circles and the line are based on theoretical calculations. The filled circles represent measured values.

Increasing the pH-value by 0.2-0.4, as happens during silica polymerization of many Icelandic geothermal waters, affects the degree of saturation for minerals that have pH-dependent solubility, such as hydroxides, calcite and magnesium silicates. Silicic acid will precipitate on any surface that bears OH groups (Iler, 1979). Precipitation of hydroxide minerals, which nucleate homogeneously in solution, produces abundant of OH-groups on their surfaces for co-precipitation of amorphous silica.

Formation of Al-silicate scales sometimes causes problems in geothermal utilization (Kristmannsdóttir, 1989; Gallup, 1997). Their solubility is not known but above a pH of approximately 7, minerals containing only aluminum and silica display increased solubility with increased pH. Increasing the pH-value would therefore decrease the risk of Al-silicate deposition.

4 Waste water from the Nesjavellir geothermal power station

Two types of wastewater come from the Nesjavellir geothermal power station, Iceland. One type is the separated water from the steam separators which is at 180° C and the other condensed steam. The separated water is cooled to about 83° C in heat exchanger and the condensed steam to about 67° C. The quantity of geothermal water and condensed steam from the power plant is roughly 300 and 150 l/s, respectively. The water from the separator has low salinity (<0.01 M) and a pH-value around 8.5 as measured at 25°C. The silica concentration is between 750 and 850 mg/kg depending on which drillholes are in production. The steam condensate has pH-value of 5.0 at 25°C and can be treated as distilled water as it has almost no dissolved material, only few mg/kg H₂S and CO₂. The water from the separator has so far been disposed of on the surface. Injection into the bedrock is not possible because at 83°C this water is amorphous silica over-saturated and silica deposition could be expected to deteriorate the injection drillhole. The condensed steam is presently injected into the ground through a shallow drillhole.

Experiments on silica polymerization for the water from the separators show that monomeric silica concentration is reduced from 744 to 474 mg/kg in one hour and to 450 mg/kg in two hours (Fig. 4). Total silica concentration did not change during the polymerization process so insignificant silica deposition took place during the experiment. The amorphous silica over-saturation is reduced during polymerization from 420 to 153 mg/kg in one hour and to 129 mg/kg in two hours. The pH increase during the polymerization process is accounted for in these calculations.



Figure 4: Changes in unionized monomeric silica concentration with time in separated water from the Nesjavellir power station.

Mixing the two types of wastewaters gives a 78°C hot mixture. Amorphous silica over-saturation in the mixture is 200 mg/kg if the silica in the water from the separator is not allowed to polymerize, but it is 22 and 6 mg/kg if the silica is allowed to polymerize for one and two hours prior to mixing, respectively. Ageing reduces amorphous silica over-saturation in the waste water ten times or more, and therefore greatly decreases potential silica deposition from the waste water. The mixture is only

slightly over-saturated and injection of this mixture back into the bedrock is unlikely to cause problems.

In this experiment the initial silica concentration was 744 mg/kg which is around the lower limits for silica concentrations in the water from the separators. Higher silica concentration would not cause problems because, as mentioned above, higher amorphous silica over-saturation increases the rate of silica polymerization.

5 Conclusion and discussion

Silica scaling is the main obstacle for efficient use of high-temperature geothermal waters. Extracting its heat is not a problem using heat exchangers, but disposal of a solution highly over-saturated with respect to amorphous silica requires special treatment. Tests show that ageing amorphous silica over-saturated geothermal waters to allow the silica in excess of amorphous silica solubility to polymerize, reduces much the rate of silica deposition. For optimizing polymerization rates, initial over-saturation can be controlled by adjusting the temperature of the water. Cooling will increase the rate of polymerization. It should though be kept in mind that increased over-saturation will also increase the risk of silica scaling.

Silica polymerization has been regarded as an precursor to silica precipitation or silica geling (Iler, 1979). The general theory of silica polymerization in the pH range 7-10 is that polymers grow in size with time. Their surfaces are negatively charged so they repel each other. Silica particle growth therefore continues without aggregation. In saline solution these repulsive forces are reduced and geling and aggregation occurs. The method presented here to reduce the rate of amorphous silica deposition from over-saturated solution does therefore not necessarily work for relatively saline geothermal waters.

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