Treatment of Geothermal Waste Water to Prevent Silica Scaling

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ABSTRACT

Silica scaling potential from geothermal waters puts limits on to what extent the heat from the water can be extracted. Once the waters become over-saturated with respect to amorphous silica, the handling of such waters becomes problematic. Many methods have been proposed to address this problem. One of them is aging the geothermal waste water allowing monomeric silica in excess of amorphous silica solubility to form polymeric silica thus reducing amorphous silica over-saturation. In geothermal water of low ionic strength polymeric silica has lesser tendency to precipitate than monomeric silica. If geothermal waste water is to be aged in a retention tank, or a pond, a good knowledge of polymerization rates are necessary. In this contribution we study the time required to lower the monomeric silica concentration in solutions initially containing 800 mg/kg silica to silica concentrations close to equilibrium with amorphous silica. We present experimental data on silica polymerization in the pH range 2.3-9.0 at 80°C and in the ionic strength range 0.024-0.50 at pH 7.13. The concentration of molybdate active silica is most reduced in solutions with pH between 7-8. At higher pH the solubility of amorphous silica increases and silica polymerization does not proceed as far as between pH 7 and 8. After one hour of polymerization solutions at pH 7-9 are close to equilibrium with respect to amorphous silica and very little is gained by aging the solution longer. Increased ionic strength speeds silica polymerization but is also enhances the rate of silica deposition.

1. INTRODUCTION

Silica concentrations in high-temperature geothermal waters are controlled by the solubility of quartz. Silica minerals, such as quartz, possess prograde solubility, and during cooling upon utilization of the geothermal water, it may become over-saturated with respect to amorphous silica. Its precipitation rate is fast and handling of amorphous silica oversaturated waste waters from high-temperature geothermal power plants can be problematic. For this reason geothermal waters are usually disposed of at temperatures above amorphous silica saturation. Several methods have been proposed to reduce the risk of silica scaling. They include decreasing or increasing the pH of the waste water (Gill, 1993; Gudmundsson and Einarsson, 1989), mixing the waste water with water with low silica concentration (Gallup and Featherstone, 1985), adding organic inhibitors (Gallup, 2002, Candelaria et al., 1996), controlled precipitation by addition of silica gel (Sugita et al., 1998 and 1999), or cationic reactant to trigger silica deposition (Ueda et. al., 2000 and 2003) and storage in a retention pond (Yanagase et al., 1970). These methods have proven successful in individual geothermal areas but no universal method has been developed to prevent silica scaling.

The only silica species in geothermal reservoir waters is monomeric. (Zotov and Keppler, 2002). When monomeric silica concentration in waters exceeds that of amorphous silica solubility, the monomeric silica has the tendency to deposit directly onto available surfaces or to react to form silica dimers, trimers and polymers. Studies have shown that polymeric silica has lesser tendency to precipitate than monomeric silica. Many studies have been performed on the rate of silica polymerization (Weres et al., 1981; Rotbaum and Rhode, 1979; Crerar et al., 1981; Gunnarsson and Arnórsson, 2003) and the rate has proved to be affected by pH-value, ionic strength, temperature and the degree of over-saturation with respect to amorphous silica. Despite many studies the mechanism of silica polymerization is not completely understood and reaction orders between 1 and 8 have been reported (Chan, 1989). Part of the problem is due to the fact that individual silica species can not been measured. The only distinction with regard to silica species can be made between molybdate active silica and total silica and the difference being considered polymeric silica. Methods have been developed to distinguish between monomeric, dimeric and trimeric silica by measuring the rate of formation of the yellow molybdosilicic complex (Alexander, 1953; Dietzel and Usdowski, 1995). These methods, however, do not work well for studying the early stages of polymerization when the polymerization rate is very fast.

Yanagase et al. (1970) reported that silica scaling in pipelines could be reduced 10 times by aging the geothermal waste water from Otake geothermal area, Japan, in a retention pond allowing the silica to polymerize. Experience at Olkaria geothermal field, Kenya shows that waste waters do not precipitate silica if stored in a retention pond before disposal into an infiltration pond (Arnórsson, 2004). Bremere et al. (2000) studied silica deposition on silica gel from over-saturated solutions at pH 7 and 25°C and found that formation of silica polymers strongly negatively affect the removal of silica from solution. From the above, it is evident that in some cases storing geothermal waste waters in a retention tank allowing the monomeric silica to form polymers, will reduce the silica scaling potential of the waste waters. If such storing is to take place as a method to lower the risk of silica scaling, good knowledge of the silica polymerization rate is necessary.

In this contribution we present experimental results of silica polymerization rates at 80°C in the pH range of 2.3-9.0 and the ionic strength range of 0.024-0.50 at pH 7.13. The focus of this study was to determine the time required to reduce considerably the monomeric silica concentrations of geothermal waters and therefore reduce the risk of silica scaling.

2. METHODS

Experiments on the rate of silica polymerization in synthetic silica solutions containing 800 mg/kg SiO_2 were

performed at 80°C in the pH range 2.3-9.0 at 80°C. Separate experiments were performed at pH 7.13 at 80°C in the ionic strength range 0.024-0.5 M with an initial silica concentration of 890 mg/kg SiO$_2$.

Silica stock solutions were prepared by dissolving silica gel in 0.1N NaOH solution at room temperature. After the dissolution, the stock solution was filtered through 0.2 µm cellose acetate filter paper and stored at room temperature. For each experimental run, a 450 ml experimental solution was prepared by dilution of the silica stock solution with deionized water and 9.0 ml 5.0N NaCl solution to obtain the desired silica concentration and ionic strength. In some cases a pH buffer was added to stabilize the pH during the experimental run. After dilution and addition of the buffer the pH of the experimental solution was between 11.5 and 12 measured at room temperature. This makes the experimental solution under-saturated with respect to amorphous silica and analysis showed all the silica to be molybdate active.

In the pH range 2.3-4 no buffer solution was added as the pH of these solutions is stable. In the pH-range 4.5-6 and 6-9 acetic acid and ammonia and were used as buffers. The buffer concentrations in the experimental solutions were 0.01M. Experimental solution were heated at 80°C for at least 24 hours prior to onset of silica polymerization by addition of HCl, to lower the pH and make the solution amorphous silica over-saturated.

Samples for silica analysis were drawn periodically from the experimental solutions with a 10 ml syringe and passed through a small cooling spiral where it was cooled to room temperature in few seconds. A portion of the cooled aliquot was extracted by pipette for analysis. Cooling of the experimental solution affects the polymerization rate. Therefore, the sampling time was kept at a minimum and the whole procedure did not take more than 30 seconds. Samples for measurements of total dissolved silica were filtered with 0.2µm cellose acetate filter, diluted 10 times and acidified with HNO$_3$.

Silica concentration was determined with molybdate method (Franson, 1985). Only monomeric silica reacts with the molybdic acid but in the analytical procedure the sample is diluted and the analytical solution becomes under-saturated with respect to amorphous silica. Once under-saturated, silica dimers and trimers break down fast enough to react with the molybdic acid and form the yellow molybdosilicic complex (Iler, 1979). It is therefore necessary to refer to molybdate active silica instead of monomeric silica when interpreting the results of this study. Total dissolved silica was measured using ICP-AES. pH was measured in cooled samples at room temperature and subsequently calculated at experimental temperature using the WATCH speciation program (Arnórsson et al., 1982) version 2A (Bjarnason, 1994), which assumes alkalinity to be preserved at all temperatures.

3. RESULTS

The rate of silica polymerization over the pH-range of this study varies very much. An example of four experiments is shown in Figure 1. A common behavior of silica in a polymerization experiment is that during the initial stages of the experiment molybdate active silica concentrations are relatively stable for some period of time before beginning to decrease. This induction period has been observed by other authors and is thought to represent the time required to form a polymers of critical size. Quantification of silica species during the induction period is difficult as the

method for analyzing silica does no distinguish between monomeric, dimeric and trimeric silica. The length of the induction period is proportional to initial silica concentration (Rothbaum and Rhode, 1979). At pH above 7, this induction period is not observed in our experiments but at pH 2.3 the induction period was 17 days (Fig. 1). After the induction period molybdate active silica stabilized at silica concentrations corresponding to the solubility of amorphous silica (Gunnarsson and Arnórsson, 2000)
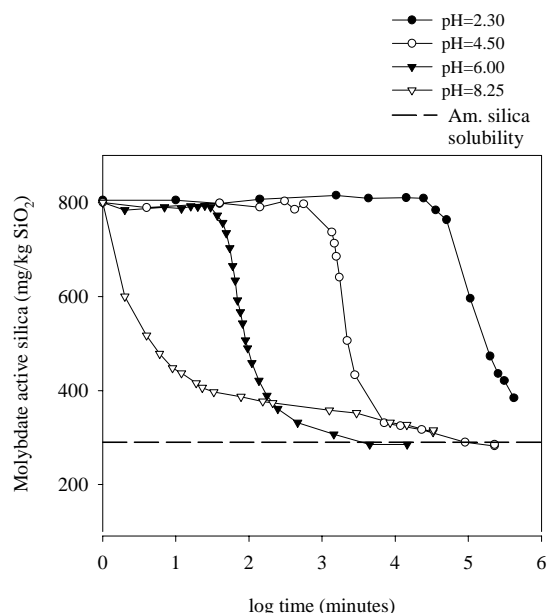

Figure 1. Behaviour of molybdate active silica in four polymerization experiments at various pH-values. Experimental temperature was 80°C and I = 0.124M.

3.1 pH-effects on reduction time

Figure 2 shows molybdate active silica concentration in solutions with various pH-values initially containing 800 mg/kg SiO$_2$ after 1, 2 and 4 hours of polymerization. The broken line represents amorphous silica solubility according to Gunnarsson and Arnórsson (2000) taking into account the formation of the H$_3$SiO$_4^-$ and NaH$_3$SiO$_4$ species. The dissociation constants for H$_4$SiO$_4$ and NaH$_3$SiO$_4$ at 80°C are from Arnórsson et al. (1982).

The pH-value of the experimental solution has a strong effect on reduction in molybdate active silica concentration after 1 to 4 hours of polymerization. The general trend is that after 1, 2 or 4 hours of polymerization molybdate active silica concentration is closer to equilibrium with respect to amorphous silica at higher pH than at lower pH. This means that solutions with high pH-values reach amorphous silica saturation faster than solutions with lower pH. Between pH 2.3 and 4.5 very little or no reduction in the molybdate active silica concentration has occurred after 4 hours reaction time. In the pH range 7-9 most of the monomeric silica above amorphous silica solubility has formed polymers 1 hour after the start of the experiment. Between 1 and 4 hours the molybdate active silica decreases insignificantly at those pH-values. Between pH 4.5 and 7 most of the silica polymerization takes place between 1 and 4 hours after the start of the experiment.
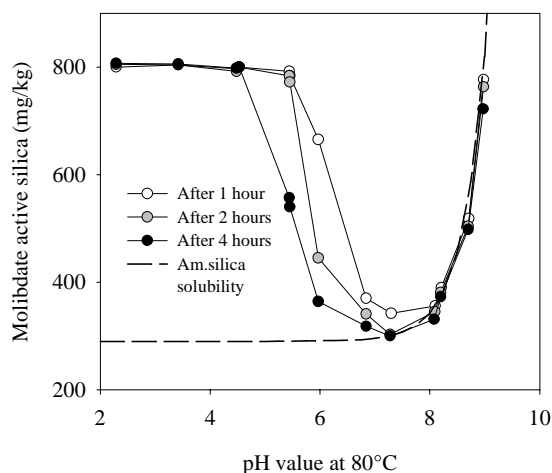
Figure 2. Concentration of molybdate active silica after 1-4 hours of polymerization as a function of pH-value. Experimental temperature was 80°C and I = 0.124M.

From Figure 2 it can be deduced that if this method of preventing silica scaling is to be applied the optimum pH of the geothermal water is above 6, as calculated at 80°C. At lower pH values the polymerization time could become too long to be a practical solution of silica scale formation from high-temperature geothermal fluids.

3.2 Effects of ionic strength

Figure 3 shows three polymerization experiments performed at 80°C but with variable ionic strength. Initial monomeric silica concentration was in all cases 890 mg/kg SiO_2. Increased ionic strength increases the rate of silica polymerization. Higher salinity also increases the risk of silica precipitation. At a pH-value above around 7, silica polymers have negative surface charge and therefore individual polymers repel each other. These repelling forces are reduced when the ionic strength is increased (Iler, 1979). The polymers grow in size and eventually become so big that they deposit. Figure 4 shows the total silica concentration in the same set of experiments as are shown in figure 3. Total silica concentration remains unchanged for 20 days of polymerization in a solution with 0.024 M ionic strength, whereas in an solution with an ionic strength of 0.124 M it remained constant for around 2 hours, before it started to decline and in an experimental solution containing 0.50M the total silica concentration was down to 282 mg/kg in one hour. In the experimental solutions with 0.124 and 0.50M ionic strength the total silica concentration stabilized at silica levels slightly below the solubility of amorphous silica (Fig. 4). This can be explained by lower solubility of amorphous silica in solutions containing high salt concentration (Marshall, 1980; Chan et al., 1987).

Applying a silica polymerization aging method to prevent silica deposition from form geothermal waste water of high ionic strength might not be successful because silica deposits might form during the aging process. This method might only be successful in geothermal waste waters of low salinity.
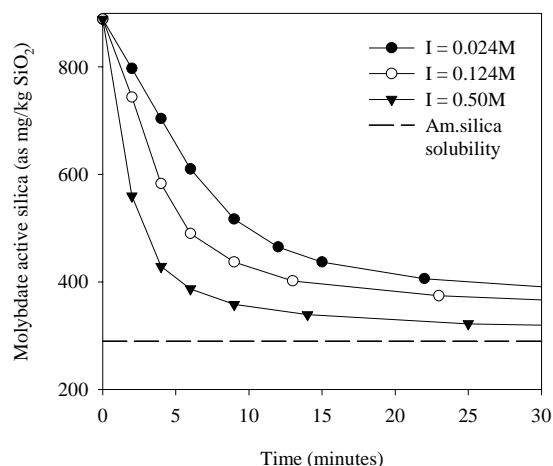

Figure 3. Silica polymerization in solutions at 80°C with initial SiO_2 concentration of 890 mg/kg at variable ionic strength. The pH of the solution was 7.13 at experimental temperature.
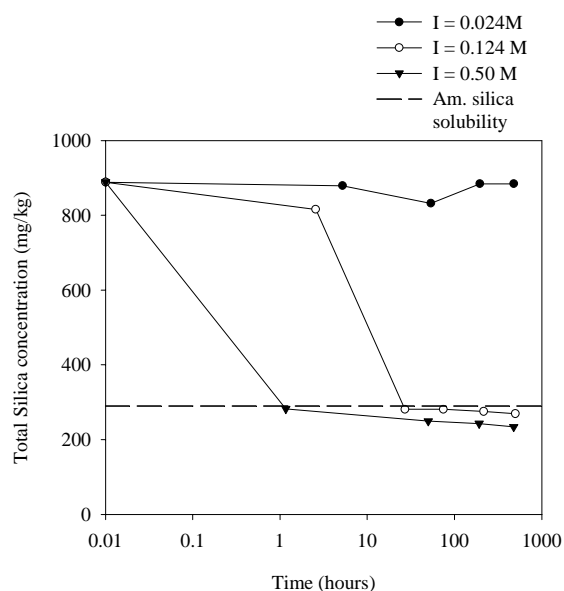

Figure 4. Total silica concentrations in experiments performed at variable ionic strength at 80°C. The pH of the solution was 8.5.

4. CONCLUSIONS AND DISCUSSION

Handling of waste water from geothermal power plants can be troublesome because of its silica scaling potential as the geothermal water cools down. Aging geothermal waste water in a retention tank or pond, allowing the monomeric silica in excess of amorphous silica solubility to form polymers, can considerably lower the silica scaling potential of such waters. If such a silica scaling prevention method is to be applied knowledge of rate of silica polymerization is very important as it determines how long the waste water has to be stored or aged.

The decrease of molybdate active silica in a solution initially containing 800 mg/kg at 80°C is at a maximum between pH 7 and 8. At higher pH the rate of silica polymerization is fast but it does not proceed as far as at

lower pH-values because considerable fraction of the monomeric silica is ionized. At pH above 7, the silica in the experimental solution stabilized at silica concentration corresponding to equilibrium with respect to amorphous silica in less than 4 hours. Increased ionic strength increases the rate of silica polymerization, but it also increased the rate of silica deposition. Therefore enhancing the rate of silica polymerization will increase the risk of silica scaling. It is therefore the relative rates of the two reactions, silica polymerization and deposition, that determine the success of the method discussed here to lower the risk of silica scaling. This method is not likely to be suitable for geothermal waters of high salinity because of the high silica deposition rate. It might as not be suited for geothermal waters with pH lower than 6 at 80°C because of slow polymerization rates. The size of a retention tank is determined by the rate of silica polymerization. If the wastewater has a pH between 7 and 8 the polymerization time is at a maximum requiring the smallest retention rank. A retention tank is a better option than a retention pond because in a retention pond oxygen has access to the waste water enhancing corrosion of the pipelines and could trigger precipitation of other minerals such as iron(III) hydroxides. Amorphous silica precipitates on any surface containing an OH-group (Iler, 1979), and formation of iron hydroxide minerals or just any hydroxide minerals can trigger silica deposition.

The method of silica polymerization to reduce the risk of silica deposition from geothermal water in environmentally friendly. It does not require additional cost except for starting cost of building a retention tank. Seeding methods and addition of an acid or a base require the production and transportation to the geothermal site of undesirable chemicals. The cost involved with the polymerization method is capital cost related to construction of a retention tank. No operational cost is involved.

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