

Silica deposition in Enhanced Geothermal Systems

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Central Australia has one of the hottest rock resources on earth, making it a potential region for developing geothermal energy using Enhanced Geothermal Systems (EGS). However, this technology is yet to be proven under local conditions and so relatively little field data or experimental data relevant to local conditions are available. Nevertheless, much can be learned from the global experience due to the operation of conventional geothermal energy plants, i.e. those using heat from volcanic activity. The amount of heat that can be extracted from high-temperature underground reservoirs using water as a working fluid in a closed loop is significantly limited by the onset of silica precipitation and subsequent scaling of heat exchanger surfaces and fouling of reservoirs as the water is cooled. The precipitation rate of amorphous silica is relatively rapid, resulting in potential deposition if the water is cooled below its saturation temperature. With the present level of understanding, experimental determination of deposition rates in individual fields is ultimately required to determine the scaling potential of a given geothermal brine. However, in the absence of such data under conditions of relevance to EGS operational conditions, a simplified mathematical approach is employed to predict the deposition rate of silica under idealised conditions. This is seen as a first step in developing a rigorous model of the behaviour of silica in EGS. Such a model would allow the optimisation of silica management strategies and allow new methods of silica removal and/or control to be devised, evaluated and assessed, prior to experimental investigations, at low cost.

Keywords: Hot dry rock, silica fouling, silica deposition rate, silica polymerization

Silica Scaling

Solid silica is present within geothermal reservoirs as quartz, and the concentration of silica in the brine at the exit of the reservoir, typically 300-700 mg/kg SiO₂, is controlled by the solubility of quartz at the reservoir temperature (Fournier and Rowe, 1966). On cooling the brine becomes supersaturated with respect to amorphous silica and silica either precipitates from the brine as amorphous silica or polymerises to form colloids which may stay in solution or may deposit onto surfaces. The fouling of heat exchanger (and other) surfaces can lead to decreased thermal efficiency, increased maintenance costs due to

cleaning and increased operational costs due to expensive abatement strategies.

The mechanism of silica precipitation and deposition is quite complex and poorly understood (Brown and Bacon, 2009). Following an induction period (Gunnarsson and Arnórsson, 2005; Bohlmann *et al.*, 1980), monomeric silica begins to polymerize. At high degrees of supersaturation, polymerisation occurs via rapid homogeneous nucleation. Supercritical silica particles grow by further reaction with silicic acid and eventually coagulate or flocculate to produce a gel, followed by a cementation of the particles in the gel by chemical bonding and further molecular deposition among the silicic acid particles (Weres *et al.*, 1982). The polymerization process will continue until the concentration of monomeric silica reduces to the saturation concentration of amorphous silica at the fluid temperature. The deposition process following the polymerized silica is known as particle deposition, which produces white, fluffy, scale with dry density of about 0.95 g/cc. At lower concentrations of dissolved silica, slow homogenous nucleation can occur with direct deposition of dissolved silica on solid surfaces being the dominant polymerisation process (Weres *et al.*, 1982). Deposits that are formed by direct precipitation of monomeric silica are more destructive and difficult to remove, producing hard, vitreous, dark coloured scale, with the density of about 2.0 g/cc. Some studies have identified that monomeric silica is more likely to precipitate and deposit than polymeric silica (Bohlmann, 1980; Gunnarsson and Arnórsson, 2005). A number of factors effect the polymerization rate of amorphous silica in geothermal brine, including pH, temperature, salt concentration, residence time, and the presence of certain ions.

Prediction of the silica deposition rate

Reinjection aquifers in Enhanced Geothermal Systems (EGS) have been considered to be the area with the greatest risk of having silica deposition problem. Predicting polymerisation and deposition rates of dissolved silica in the EGS reinjection aquifer is complex due to a lack of data from operating sites. A number of factors should be taken into account in modelling the real conditions, such as fluid mechanics, heat and mass transfer. Here we have taken a very simplified approach using experimental data for the precipitation of monomeric silica obtained under ideal conditions.

A schematic diagram of the system model is shown in Figure 1. A closed loop binary cycle is assumed with a reservoir depth of 5000 m. Only the flow of brine in the reservoir and through the heat exchanger (30 m length) is considered. Water exits the heat exchanger at temperature $T_{s1} = 90^\circ\text{C}$ and is returned to the reservoir, via the reinjection well. The brine is heated to temperature $T_R = 270^\circ\text{C}$ at the exit of the reservoir and returns to the surface reaching the heat exchanger at temperature $T_s = 260^\circ\text{C}$. The temperature profiles in the production well (2°C/km) and heat exchanger (5.67°C/m) are assumed to be linear. The temperature profile in the reinjection well is calculated using simple heat transfer assumptions and follows the method of Yu et al. (2009).

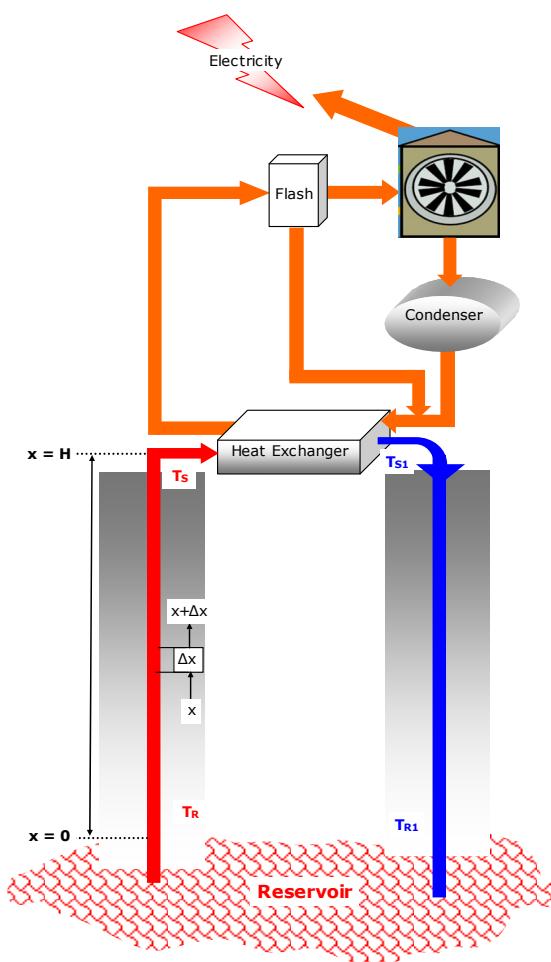
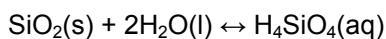


Figure 1: Schematic diagram of the mathematical simulation

The kinetics of amorphous silica precipitation have been determined by Rimstidt and Barnes (1980) for 0–300°C. For the reversible reaction:



the net precipitation rate, for dilute solutions, may be expressed as:

$$r'_{\text{SiO}_2} = -k_+ (1 - Q/K) \quad \text{mol.L}^{-1}.\text{s}^{-1}$$

where k_+ is the forward rate constant, K is the equilibrium constant and Q is the activity quotient:

$$Q = (a_{\text{H}_4\text{SiO}_4}) / (a_{\text{SiO}_2})(a_{\text{H}_2\text{O}})^2$$

where a_i is the activity of species i . The quantity Q/K indicates the degree of saturation or the *saturation ratio* (S).

Rimstidt and Barnes (1980) provide expressions for k_+ and K , as a function of temperature allowing the precipitation rate of amorphous silica to be simply calculated as a function of temperature and the concentration of silica in solution. Here, silica in solution is assumed to be in equilibrium with solid quartz at the reservoir temperature and its concentration is determined using the expression of DiPippo (2008).

The precipitation rate of amorphous silica is plotted in Figure 2 as a function of temperature and for silica concentrations of 550, 675, 745 and 800 ppm, which correspond to quartz equilibrium concentrations at reservoir temperatures of 270, 300, 320 and 340°C, respectively. As temperature decreases, the degree of saturation, S , increases and so the predicted precipitation rate increases until a maximum is achieved. With further decrease in temperature, the forward rate constant (k_+) decreases faster than S and so the net rate of precipitation decreases. As a consequence, for temperatures below about 50°C, the precipitation rate is small, despite the large extent of supersaturation and this, potentially, provides a mechanism by which silica deposition may be controlled or minimised.

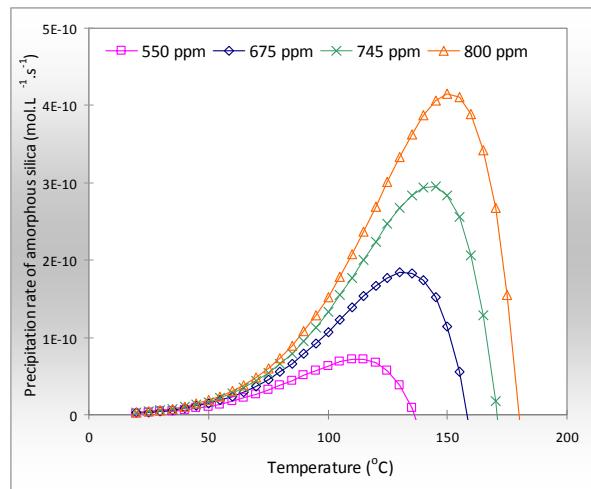


Figure 2: Precipitation rate of amorphous silica as a function of temperature and silica concentration.

Simulation results and discussion

The precipitation rate of silica in the heat exchanger is plotted in Figure 3 as a function of heat exchanger tube length. At the heat exchanger inlet, the geofluid temperature is well above the saturation temperature and the

precipitation rate is negligible. As the temperature decreases below 140°C, which occurs at approximately 22 metres, the geofluid becomes saturated with respect to amorphous silica and the precipitation rate increases substantially. The highest rate of precipitation in the heat exchanger occurs at 26 metres, corresponding to a temperature of 113°C. Thus, the final 25% of the heat exchanger is susceptible to fouling due to silica deposition.

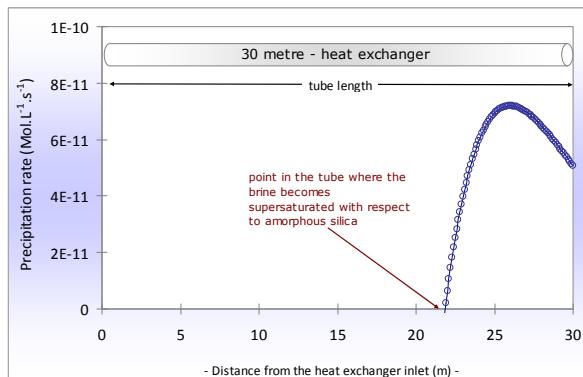


Figure 3: Precipitation rate as a function of temperature in the heat exchanger for $[\text{SiO}_2] = 550 \text{ ppm}$

The precipitation rate of silica and the geofluid temperature in the reinjection well is plotted in Figure 4. At shallow depths, the geofluid in the reinjection well continues to cool due to the lower temperature of the surrounding earth. The precipitation rate of silica decreases accordingly and reaches a local minimum at a depth of 330 m corresponding to a minimum temperature of 83.3°C. With increasing depth, the precipitation rate increases to a maximum at a depth of 1350 m, which occurs at a temperature of approximately 112°C and corresponds to the maximum precipitation rate for $[\text{SiO}_2] = 550 \text{ ppm}$ shown in Figure 2. At greater depths, the temperature increases further and the precipitation rate decreases as the extent of supersaturation decreases. Thus, the upper 30% of the reinjection well is susceptible to fouling due to silica precipitation.

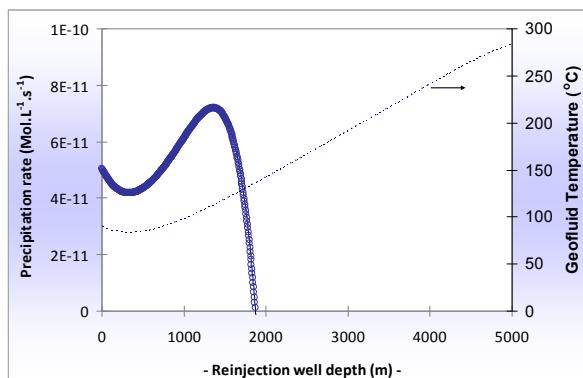


Figure 4: Precipitation rate and geofluid temperature (RH axis) as a function of depth in the reinjection well for $[\text{SiO}_2] = 550 \text{ ppm}$

Silica polymerisation

The disappearance of monomeric silica from solution may also occur via a polymerisation reaction that proceeds quite rapidly following an initial induction period. Bohlmann *et al.* (1980) report that the induction period, τ_i , may be calculated as a function of the supersaturation ratio and the pH of the solution as:

$$\ln \tau_i = \left[\ln \frac{1}{\ln(C/C_e)} \right]^8 + 4.8 - 2.3(\text{pH} - 4.5)$$

Figure 5 is a plot of the calculated induction period, as a function of the supersaturation ratio, for pH = 5, 6 and 7. At any supersaturation ratio above about 1.5, the induction period is quite rapid and occurs in less than 1 minute for neutral pH. Thus, the polymerisation of silica is expected to contribute substantially to the precipitation of silica from solution.

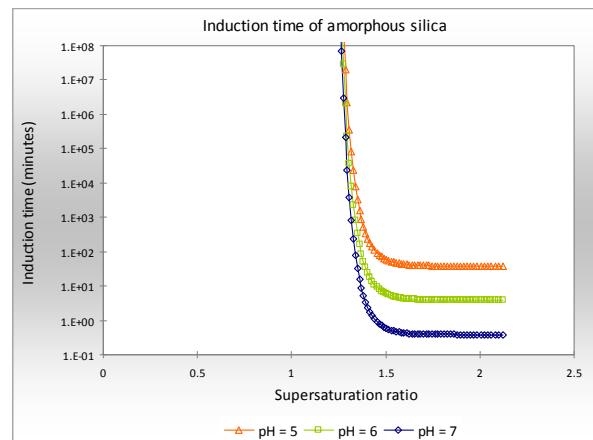


Figure 5: Calculated induction period for amorphous silica as a function of supersaturation ratio and pH

The present study assumes that amorphous silica in solution is removed primarily via precipitation of monomeric silica. The rapid induction times indicated in Figure 5 suggest that under at least some conditions the polymerisation reaction will be a significant contributor to the removal of silica. Thus, there are limitations of the present work when applying these calculations directly to practical enhanced geothermal systems. Furthermore, theoretical based models of precipitation, such as those of Rimstidt and Barnes (1980) that have been determined in the laboratory under ideal conditions, predict rates that are about three orders of magnitude slower than rates observed in the field (Carroll *et al.*, 1998).

The present work may be considered as a preliminary step towards the development of a more rigorous model of silica behaviour in EGS. Future work will include a more detailed description of the precipitation and polymerisation rates, based on empirical relationships

determined under more realistic conditions (e.g. Bohlmann *et al.*, 1980 and Weres *et al.*, 1981).

Summary

Silica deposition occurs both via direct precipitation of amorphous silica and polymerisation of dissolved silica to form colloids. In both cases, the final solid product may lead to persistent deposits on heat exchanger surfaces or to fouling of the reservoir due to entrainment of fine particles. Precipitation rates have been calculated as a function of temperature in the heat exchanger and reinjection well for conditions corresponding to a typical EGS installation. The maximum rate of precipitation occurs towards the end of the heat exchanger and in the upper section of the reinjection well, at depths above about 1350 m. Due to high geofluid temperatures, the precipitation rate is calculated to be negligible at depths below 2000 m in the reinjection well. In this study, the rate of precipitation has been calculated based on laboratory data obtained under ideal conditions and the rate of polymerisation has been neglected. Future work will include more detailed descriptions of precipitation and polymerisation based on empirical measurements.

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