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Prediction of silica precipitation rates in EGS

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Abstract

Enhanced Geothermal Systems (EGS) are an innovation in geothermal energy with a promising future in Australia. For existing geothermal power plants using hydrothermal resources, silica precipitation and deposition in plant equipment is a well-known problem. Past research on the problem enables a prediction of the level of silica precipitation that can be expected for EGS. This report provides that prediction based on the method of Weres et al. [1]. It is found that silica precipitation in EGS plants is likely to be relatively mild, primarily since EGS resources are not likely to exceed temperatures of 280°C and secondly since the salinity of EGS geofluids is expected to be moderate. Acidification and salinity reduction of geofluids are expected to be sufficient measures to control silica precipitation in EGS.

CONTENTS

Abstract.....	1
1 Introduction.....	3
2 Base case.....	4
3 Binary plants.....	4
3.1 Hard scale formation by molecular deposition	4
3.2 Colloid formation.....	7
3.3 Summary for binary plants.....	9
4 Flash plants.....	10
4.1 Summary for flash plants	13
5 Concluding remarks.....	13
Acknowledgements.....	13
References.....	14

1 Introduction

Silica precipitation in geothermal systems is caused by supersaturation of dissolved silica in geofluids. The extent of supersaturation is expressed by the supersaturation ratio, S , defined as the present concentration of silica divided by the equilibrium concentration, which for silica is mainly a function of temperature, pH and the concentration of salts. Thus, supersaturated geofluids will have $S > 1$ and precipitation will occur until such time as the equilibrium concentration is reached ($S = 1$).

In the geothermal reservoir, silica dissolves from quartz into the geofluid at high temperatures. In general, by the time the geofluid arrives at a production well the silica in the geofluid is in equilibrium with quartz and thus at an equilibrium concentration. In the power plant, the hot geofluid is cooled or flash-boiled. This may cause the dissolved silica to exceed the equilibrium concentration for amorphous silica, in which case the dissolved silica is supersaturated and will begin to precipitate. Note that the equilibrium silica concentration, at a given temperature, for amorphous silica is greater than quartz.

Problems with silica precipitation in geothermal power plants can be classified by plant;

- Binary plants, eg. organic Rankine cycles (ORC) and the Kalina cycle
- Flash steam plants

and the type of precipitation;

- Molecular deposition, ie. hard scale formation on surfaces
- Colloidal particle formation ("polymerization") and subsequent deposition

In binary plants, the geofluid is cooled as a liquid without inducing any vapour formation. Supersaturation of dissolved silica occurs due to cooling only. Flash steam plants boil the geofluid by reducing its pressure, thus concentrating dissolved silica in the liquid phase. Dissolved silica in flash plants becomes supersaturated due to both cooling and increased concentration.

Molecular deposition occurs by the reaction of dissolved silica in the form of silicic acid, $\text{Si}(\text{OH})_4$, and silicate ions, $\text{SiO}(\text{OH})_3$, with $-\text{O}-$ and $-\text{OH}$ groups on solid silica and iron surfaces. The rate of deposition depends on temperature, pH, S and geofluid salinity. Molecular deposition forms hard, vitreous, and often dark colored scales on equipment surfaces [4].

Colloidal particle formation begins with a process called homogeneous nucleation, where silica polymers develop spontaneously in solution. An "induction period" for homogenous nucleation is observed wherein a population of nuclei grows to a critical size. The dissolved silica concentration appears to change little during this time. Nucleation proceeds smoothly into a period of rapid polymer growth where dissolved silica precipitates rapidly onto the surface of the nuclei to form colloidal particles. These particles may subsequently deposit on plant or well bore surfaces. Molecular deposition of silica on deposited particles can cement them to surfaces and to other particles.

The induction period for homogenous nucleation depends greatly on the supersaturation ratio, often being instantaneous when S is initially 2 to 2.5, but lasting minutes to hours at low supersaturation and/or pH [4].



Prediction of silica precipitation rates in EGS

The induction period is practically important, as it may be prolonged to enable supersaturated geofluid to pass through surface plant and down injection wells to the reservoir without colloid formation occurring.

For most geothermal systems, silica precipitation is controlled either by maintaining the geofluid above the amorphous silica saturation temperature, or by acidifying the geofluid. The disadvantage of the former strategy is that less energy can be generated from the geofluid than would otherwise be possible. Geofluid acidification aims to reduce the molecular deposition rate and prolong the induction period for colloid formation. It has been successfully employed as described by Gallup [6].

Weres et al. [1] describe a method for predicting the rate of silica precipitation in geothermal systems based on their previous experimental results [2,2]. The method accounts for the main known effects of temperature, pH and salinity, and is acknowledged as capable of giving reasonable predictions of scaling rates under field conditions [4].

There is currently no published information on the silica precipitation rates which are likely to occur for EGS. The aim of this report is to apply the method of Weres et al. [1] to predict these rates for expected EGS operating conditions.

2 Base case

To investigate the effect of reservoir temperature, salinity, and pH on precipitation rate, we will assume a base case as given below.

Reservoir temperature:	240 C
NaCl content:	17.5 g/L (50% of seawater)
pH:	7.0

3 Binary plants

3.1 Hard scale formation by molecular deposition

In Figures Figure 1-Figure 3 the molecular deposition rate in millimeters per year is plotted against the temperature that the geofluid is cooled to as it travels through the tubes of a heat exchanger. Each temperature on the horizontal axes therefore corresponds to a physical point in a heat exchanger.

Molecular deposition on heat exchanger tubes removes negligible silica from solution, but can cause a significant thickness of scale to develop over time. Figure 1 shows the molecular deposition rate versus geofluid temperature in a heat exchanger for several reservoir temperatures. Increasing the reservoir temperature has a large effect on molecular deposition due to the increase in dissolved silica in the geofluid. The maximum scaling rate increases roughly exponentially with reservoir temperature. Increasing reservoir temperature also increases the range of geofluid temperature over which scaling occurs.

Figure 2 shows how reducing pH significantly decreases scaling. It is not possible to show effects at pH > 7, since the calculations do not account for the increased quartz solubility in this pH range.



Prediction of silica precipitation rates in EGS

Figure 3 shows that decreasing salinity reduces scaling, but not in direct proportion.

It should be noted that molecular deposition rates in practice may differ from those observed in controlled laboratory experiments such as those of Weres et al. Carroll et al. [5] observed up to 400 times higher rates of molecular deposition in field experiments compared with corresponding laboratory experiments. It was concluded that the field rates were controlled by surface defect/surface nucleation processes, whereas the laboratory rates were controlled by elementary reaction rates at the solid-solution interface. In the field experiments, the accumulation in the solid of aluminium from solution may have contributed to the higher rate.

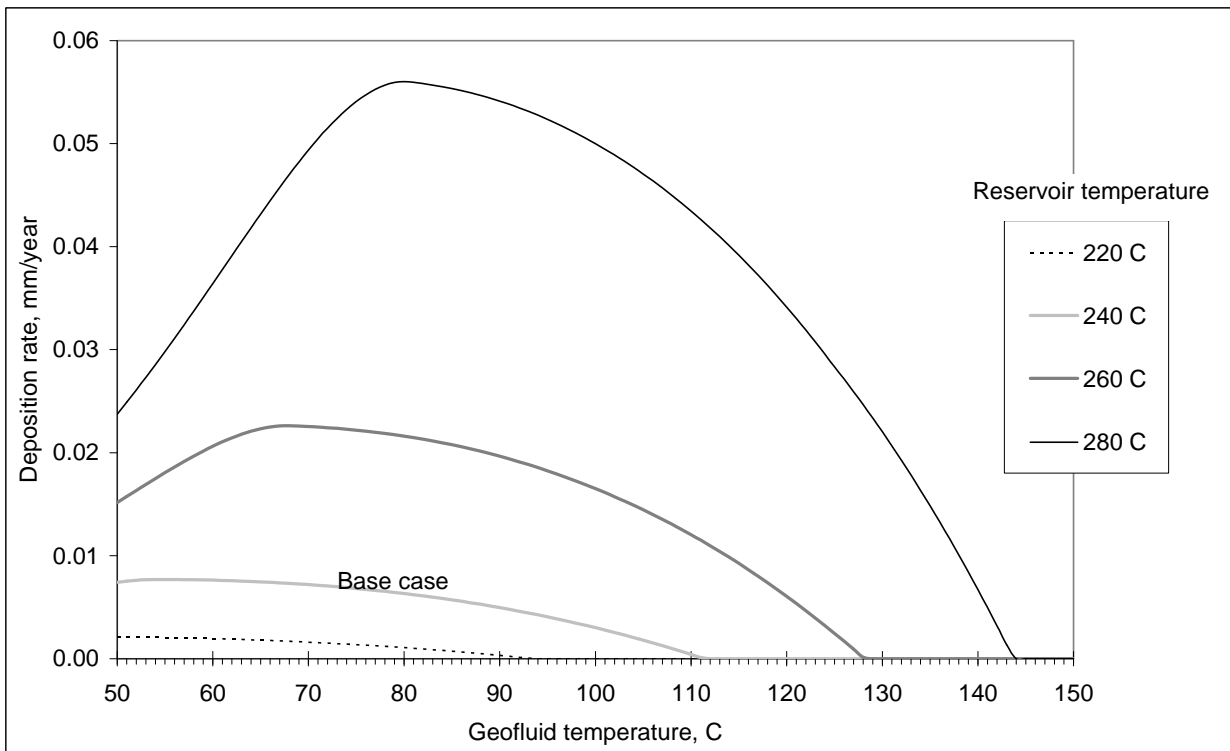


Figure 1: Molecular deposition rate versus geofluid temperature in heat exchanger - effect of reservoir temperature.

Prediction of silica precipitation rates in EGS

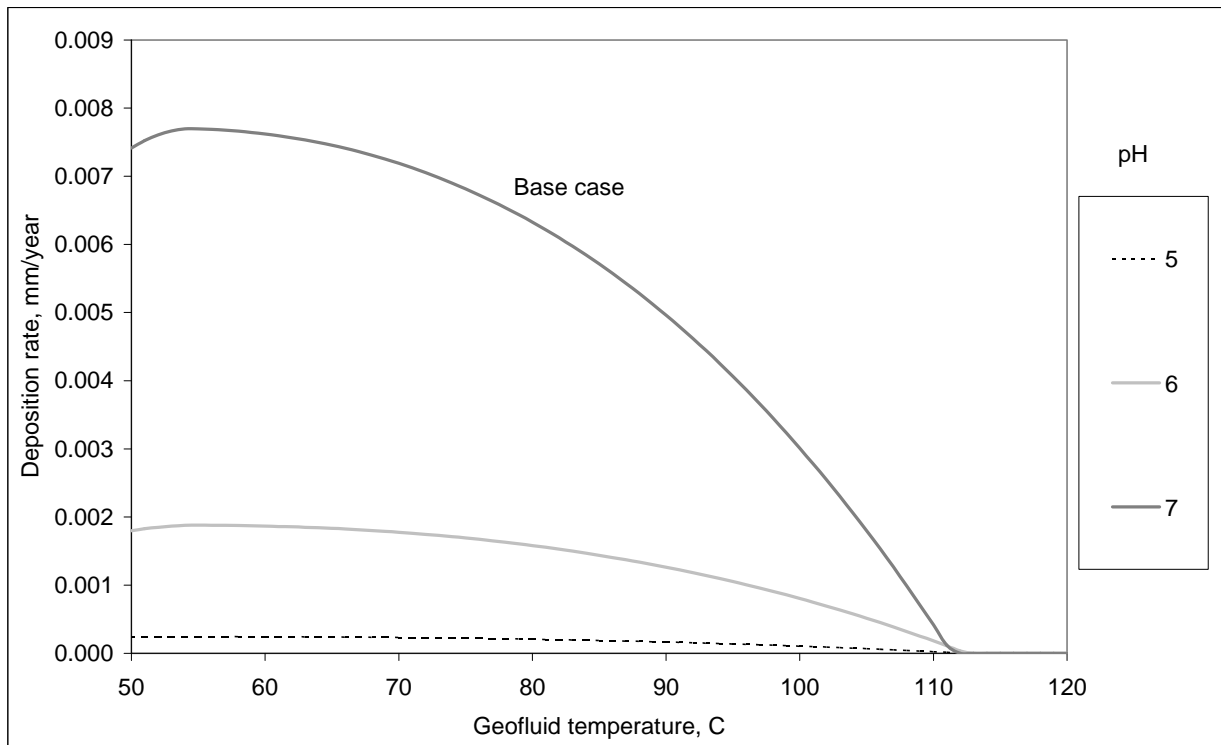


Figure 2: Molecular deposition rate versus geofluid temperature in heat exchanger - effect of pH.

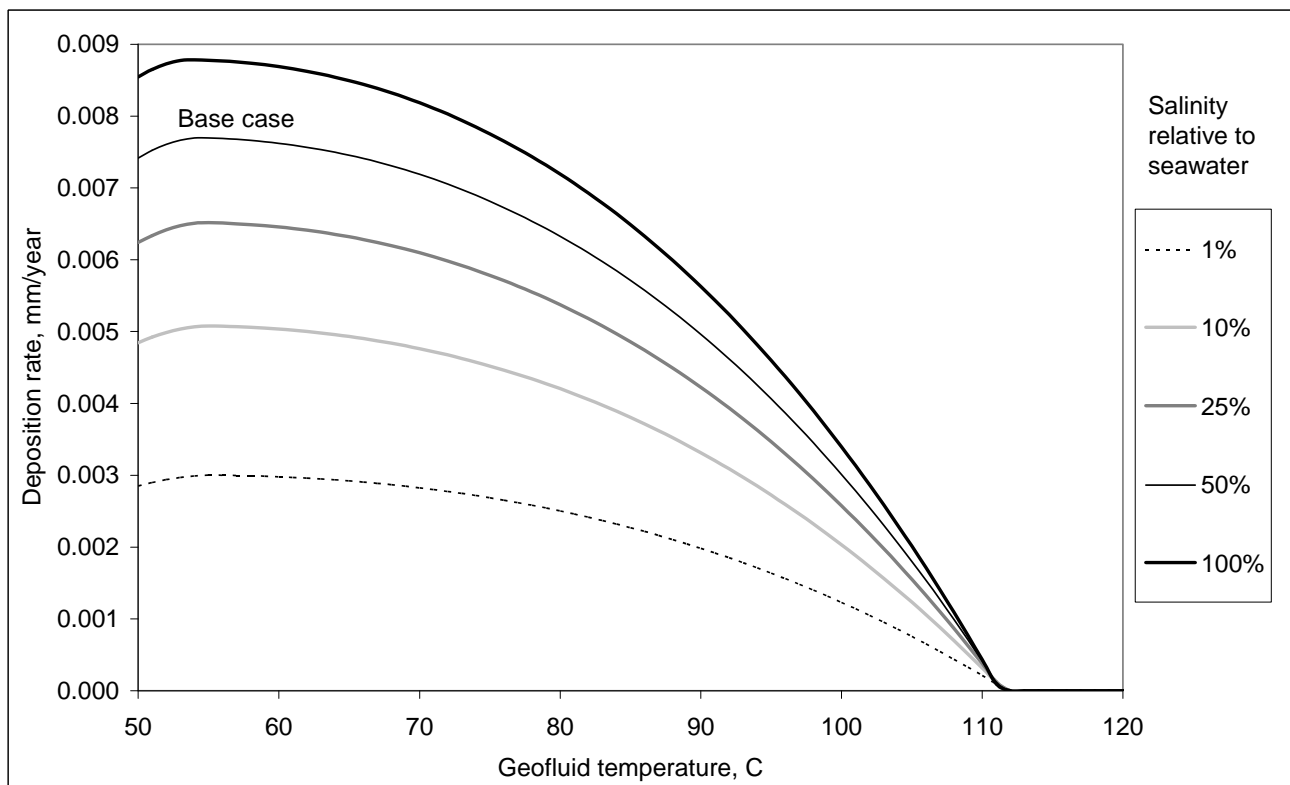


Figure 3: Molecular deposition rate versus geofluid temperature in heat exchanger - effect of salinity.

3.2 Colloid formation

Colloid formation by homogenous nucleation generally requires silica supersaturation ratios (S) greater than 2.5 to take place at significant rates. Weres et al. provides a procedure for predicting the course of colloid formation by homogeneous nucleation, but it is limited to minimum S values as shown in Figure 4. Below these minimum S values, colloid formation is likely to be dominated by heterogeneous nucleation. Also in Figure 4 are the S versus T curves values resulting from various reservoir temperatures (salinity and pH set at base case values). It is clear that under most circumstances geofluids in binary plants will not be supersaturated enough to promote significant homogeneous nucleation. Only if geofluids from very hot reservoirs are cooled to low temperatures will the minimum conditions be met according to the criteria of Weres et al. However, colloid formation at lesser supersaturation ratios may be heterogeneously nucleated by small particles in the geofluid. The occurrence of this mode of silica precipitation will depend on the specific geofluid and its likelihood can only be assessed experimentally.

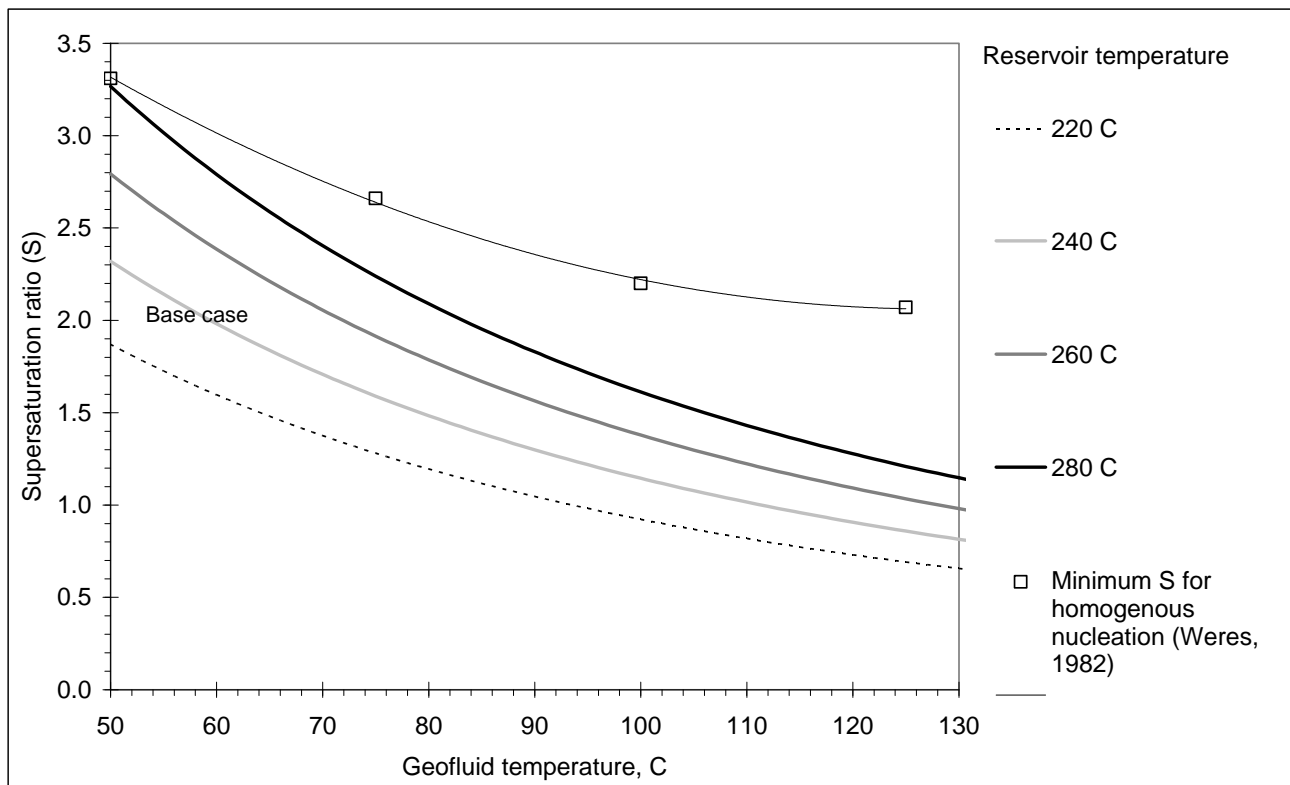


Figure 4: Supersaturation ratio versus geofluid temperature in heat exchanger.

Despite the geofluids of interest being generally unaffected by homogenous nucleation, we will briefly discuss main effects. Homogenous nucleation is accelerated by increases in supersaturation ratio, temperature, pH, and salinity. Weres et al. conducted experiments using combinations of these parameters which would give measurable changes in reasonable time-frames. The results could be reasonably reproduced by their SILNUC model, and a practical method for predicting the course of colloid formation was subsequently proposed. The method consists of shifting the time-scale of a given reference curve. Figure 5 shows a typical result, where the course of colloid formation is predicted for a geofluid at 50 °C with an initial supersaturation ratio of 3.3. There is a period of roughly 10 minutes where there is no change in dissolved silica. It is this 'induction period' which should be extended in order to avoid colloid formation.

Prediction of silica precipitation rates in EGS

In the Weres method, the time scale of colloid formation at a particular temperature and silica concentration is a function of pH and salinity. The induction period for a geofluid at 50 °C and supersaturated by a factor of $S = 3.3$ is shown in Figure 6 with respect to pH and salinity.

The geofluid may spend tens of hours at low temperature after injection to an EGS reservoir. This would suggest that the prevention of colloid formation in the reservoir would probably require a pH of 6 or less, with the appropriate value depending on geofluid salinity. There is an economic benefit in acidifying the geofluid as little as possible, therefore some EGS reservoirs may need to be 'flushed' for a period in order to remove salt in the native fluids.

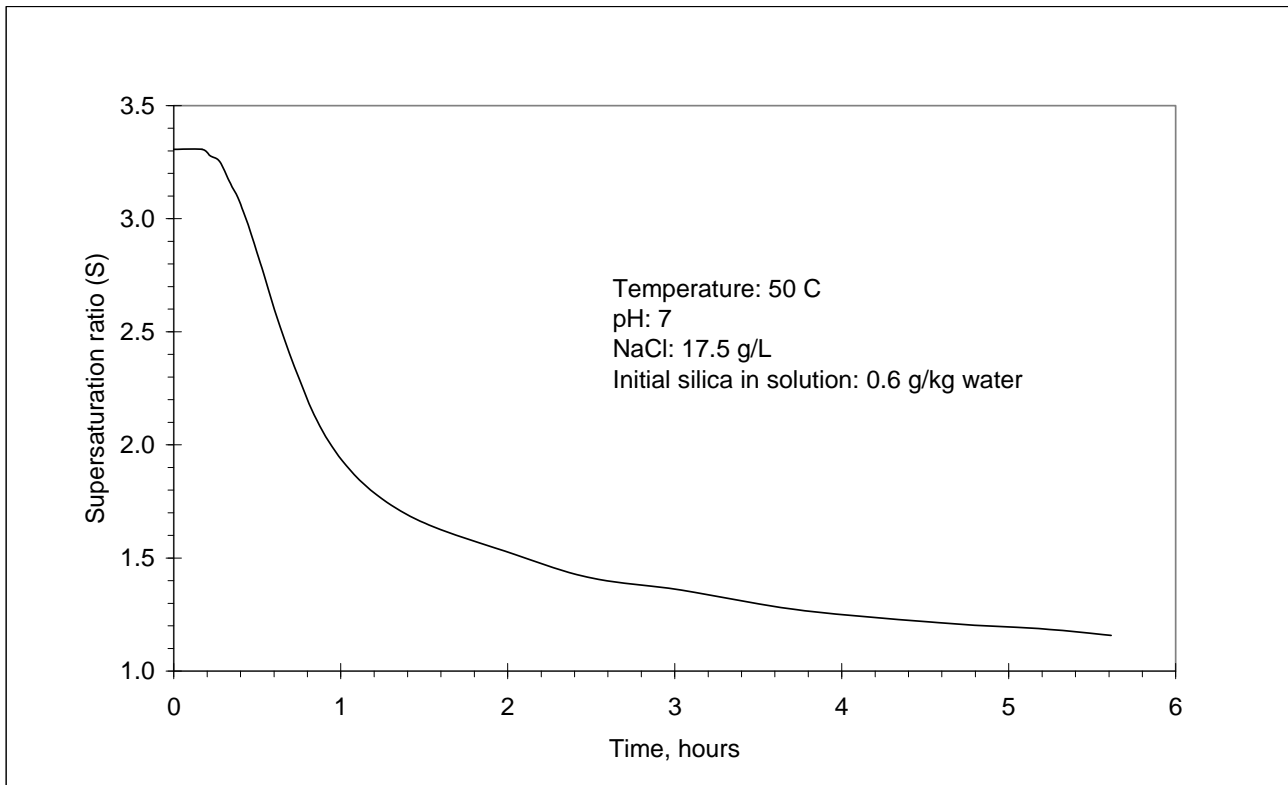


Figure 5: Supersaturation ratio versus time for a geofluid with initial $S = 3.3$, 17.5 g/L NaCl and pH = 7.

Prediction of silica precipitation rates in EGS

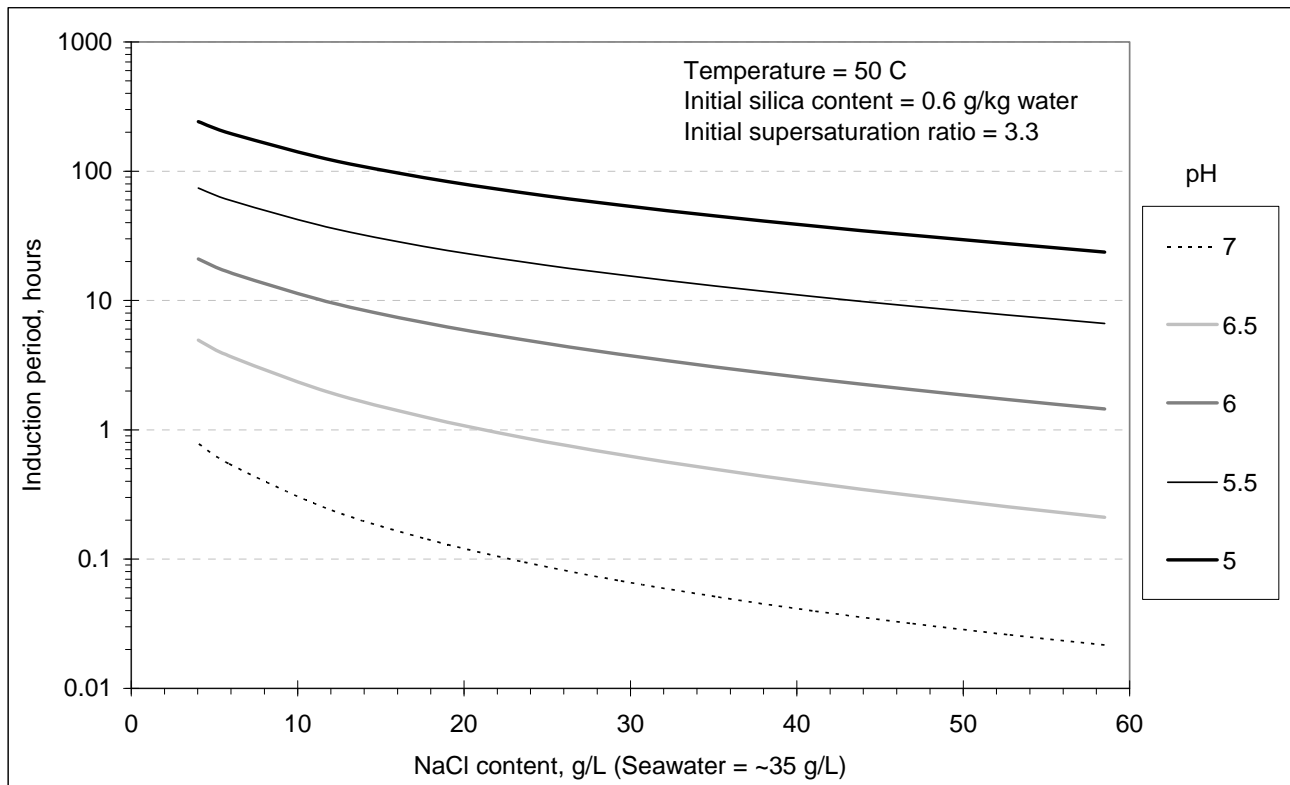


Figure 6: Induction period for colloid formation versus salinity and pH for a geofluid at 50 C and initial $S = 3.3$.

3.3 Summary for binary plants

- Formation of hard scale on plant surfaces by molecular deposition occurs at a rate that increases exponentially with reservoir temperature. At reservoir temperatures less than 220 °C, hard scale formation is relatively insignificant.
- Formation of colloidal silica by homogeneous nucleation requires a level of supersaturation that will not be encountered in most EGS binary plants. However, heterogeneous nucleation by small particles in the geofluid is possible and should be assessed experimentally.
- Both hard scale and colloidal silica formation can be mitigated by decreases in pH and salinity. With appropriate measures, it should be possible to cool geofluids to 50 °C in a binary plant without significant silica precipitation.

4 Flash plants

The assessment of flash plants assumes a double-flash plant is used, with the temperature of each flash stage set to maximise the gross power of the plant. The flash temperatures and resulting vapour fractions are shown in Table 1 for a number of assumed reservoir temperatures. In each case, the liquid in the first flash stage is under-saturated with silica. Therefore we need only be concerned with liquid in the second flash stage and liquid for re-injection.

Table 1: Double-flash plant specifications

Reservoir temperature °C	First flash stage		Second flash stage		Geofluid injection temperature °C
	Temperature °C	Vapour fraction	Temperature °C	Vapour fraction	
200	136	0.11	85	0.09	77
220	148	0.13	91	0.11	80
240	161	0.15	97	0.12	82
260	174	0.17	103	0.14	85
280	187	0.20	108	0.15	86
300	201	0.22	114	0.17	88

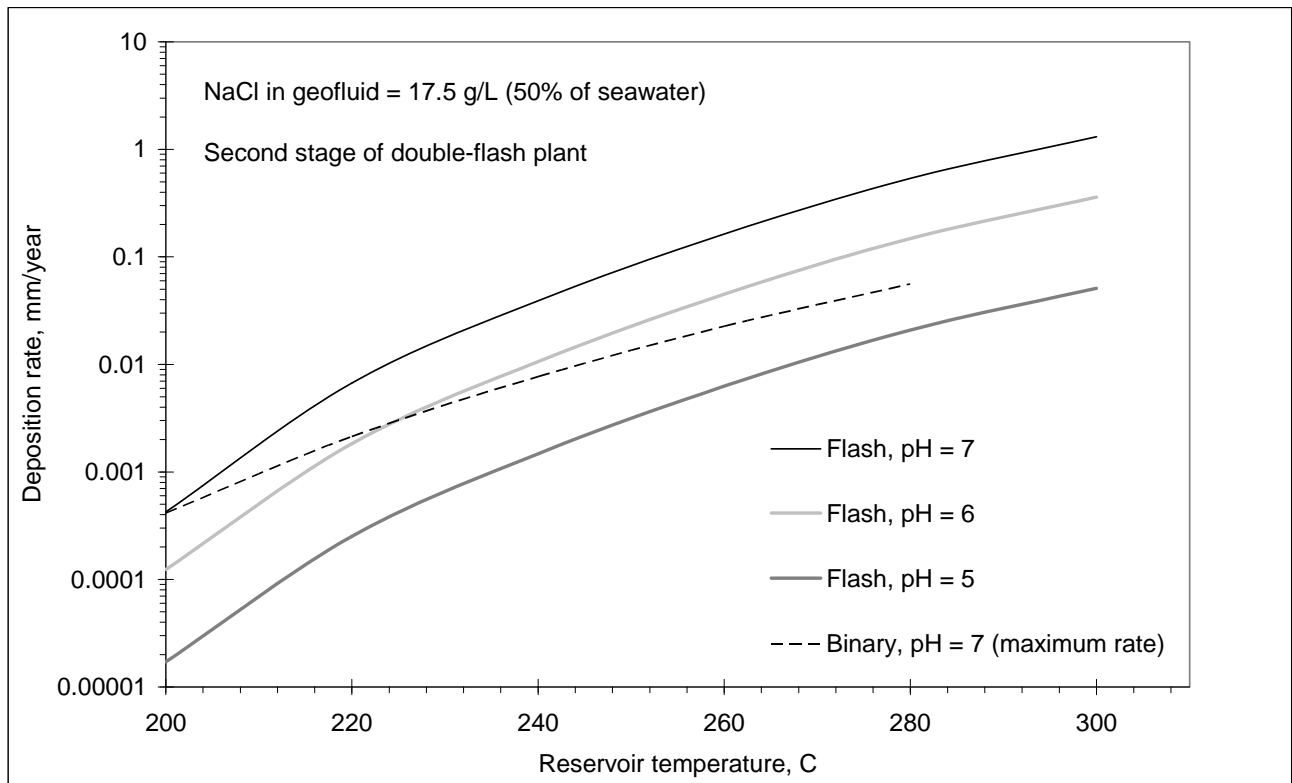


Figure 7: Rate of molecular deposition versus reservoir temperature and pH for second flash stage of double-flash plants.

Prediction of silica precipitation rates in EGS

Figure 7 shows the molecular deposition rate in the second stage of double flash plants with respect to reservoir temperature and pH. The maximum rate in binary plants at pH = 7 is also shown for comparison. The results suggest that hard scale formation in the second flash stage can be significant at higher reservoir temperatures.

Figure 8 shows the supersaturation ratio in the second flash stage versus its temperature, and the minimum S versus T curve for colloid formation as suggested by Weres et al. The intersection of these curves suggests that colloidal silica will be formed when the reservoir temperature is 280 °C or more. The S versus T curve for the injection fluid is also included in the figure and will be discussed further on.

Figure 9 shows the induction period for colloid formation versus salinity and pH for the second flash stage of a double-flash plant using geofluid from a reservoir at 280 °C. The results suggest that colloid formation is fast at neutral pH, with the induction period being ~11 minutes for a geofluid containing 3 g/L NaCl.

The second flash stage liquid is mixed with cooler condensate before being re-injected, diluting the dissolved silica. For the double flash plants investigated, the supersaturation ratios in the fluid injection line are insufficient for colloid formation by homogeneous nucleation (the 300 °C reservoir case comes close). Hence, the flash liquid needs only to be acidified enough to prevent colloid formation up to the point of mixing with condensate.

Figure 10 shows the molecular deposition rate in the injection line after the second flash stage liquid is combined with condensed steam. At the same pH, this rate is substantially less than the rate in the second flash stage and is not greater than the maximum rate expected in a binary plant.

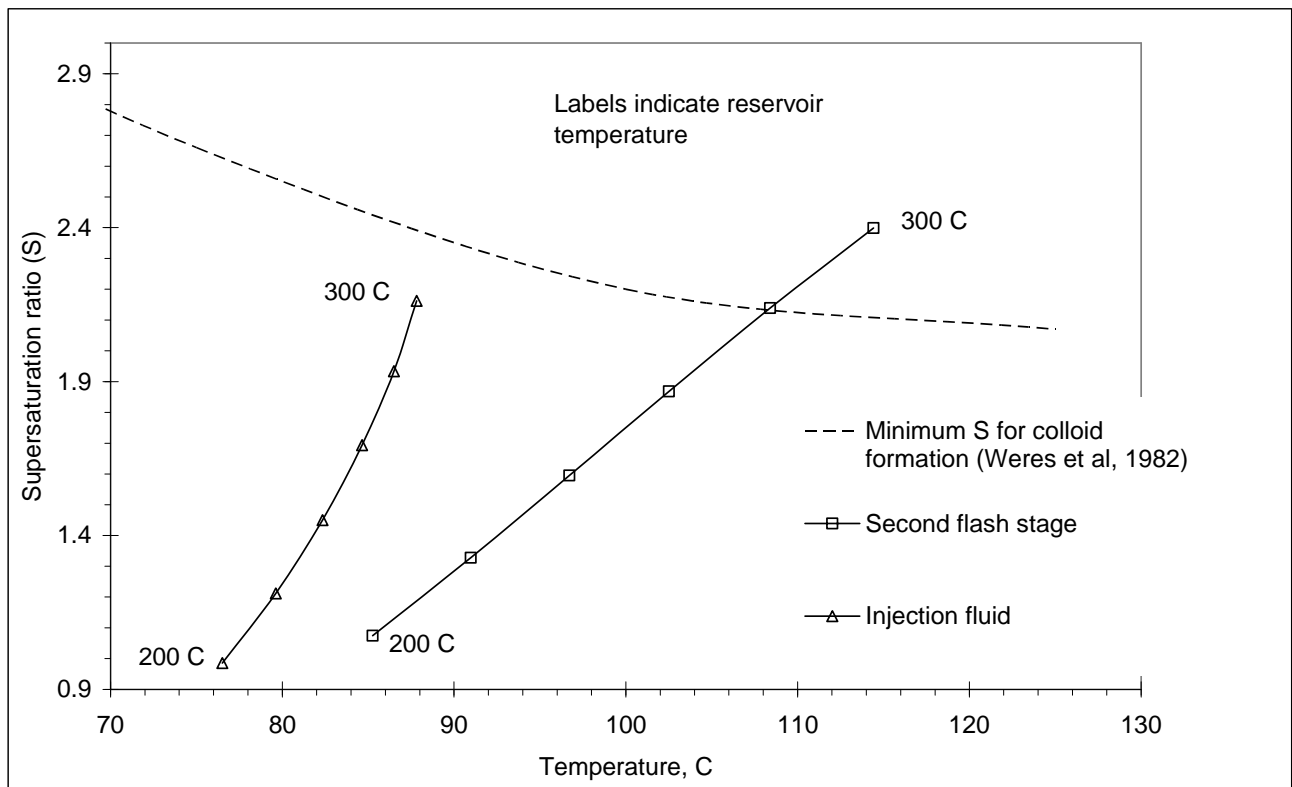


Figure 8: Supersaturation ratio versus temperature in second flash stage of double-flash plant.

Prediction of silica precipitation rates in EGS

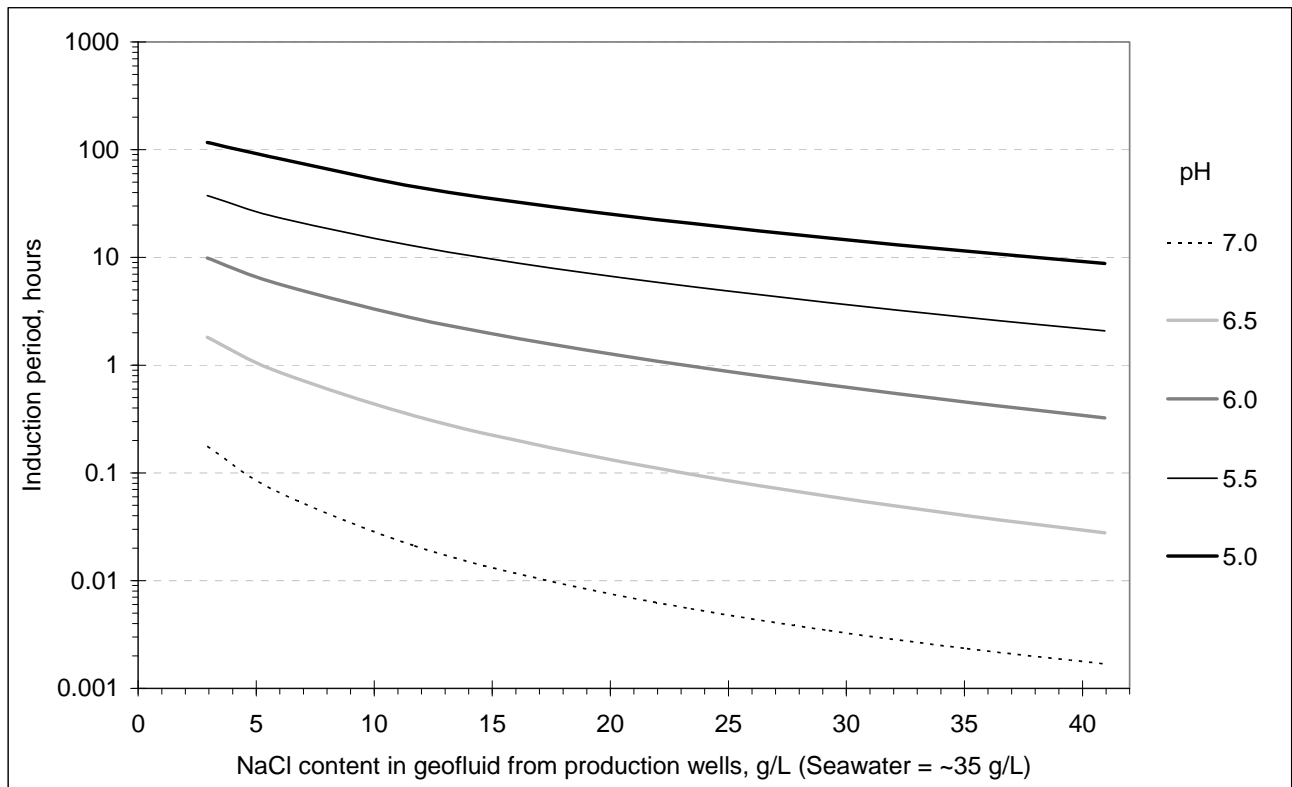


Figure 9: Induction period for colloid formation versus salinity and pH for the second flash stage of a double-flash plant using geofluid from a reservoir at 280 C.

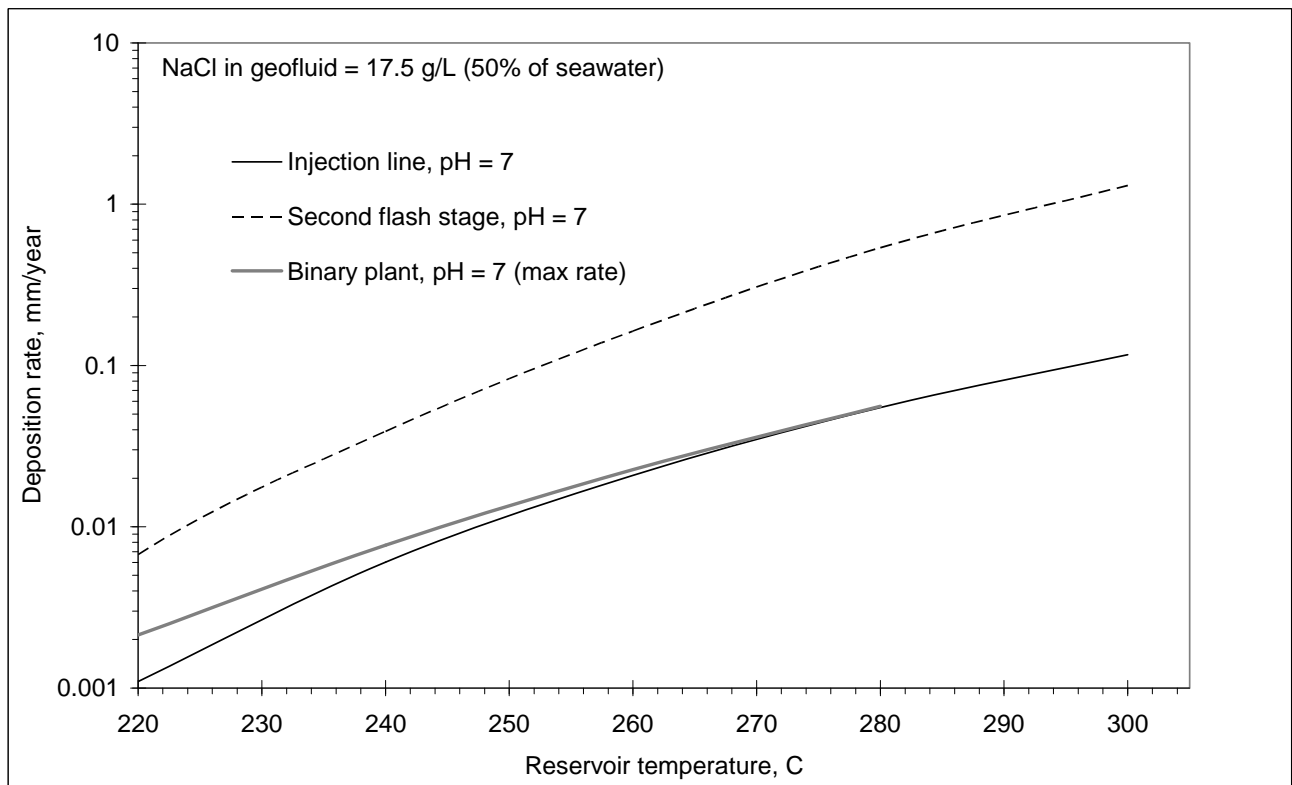


Figure 10: Molecular deposition rate versus reservoir temperature for injection line and second flash stage of double-flash plant.

4.1 Summary for flash plants

- Compared with binary plants using the same geofluid, silica precipitation problems are more severe for flash plants, due to the increase in silica concentration caused by flashing.
- In double flash plants, the first flash stage will not be affected by silica precipitation. In the second flash stage, there is potential for significant hard scale and colloid formation. Both may be mitigated by reducing pH and salinity.
- In the fluid injection line, hard scale will form at roughly the same rate as the maximum rate encountered in binary plants using the same geofluid. The injection line fluid is not supersaturated enough to initiate significant colloid formation.

5 Concluding remarks

For most EGS projects in Australia, we would expect relatively mild problems with silica precipitation in surface equipment and injection bores since EGS reservoir temperatures will probably be only 280°C or less. Moderate geofluid salinities in EGS will also limit silica precipitation rates. Geofluid acidification and salinity reduction are expected to be adequate measures to avoid problematic scaling rates.

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