

Control of Magnesium Silicate Scaling in District Heating Systems

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ABSTRACT

Magnesium-silicate scaling has been encountered in several geothermal district heating systems in Iceland. The scaling occurs in heated freshwater that has undergone thermal deaeration and also when geothermal and fresh waters are mixed.

The solubility and precipitation rate of amorphous magnesium-silicate in district heating water was studied experimentally in the temperature interval of 60 to 120 °C. The scale forming mineral was found to be amorphous magnesium-silicate, and the solubility to be controlled by the concentration of magnesium, silica and the pH of the water. The rate of mineral formation was found to be dependent on supersaturation, temperature and flow conditions.

The results have made possible the prediction of scaling when geothermal water is mixed with deaerated fresh water and have led to the abandonment of earlier plans by Reykjavik District Heating to mix geothermal water from low temperature fields and heated freshwater from the high-temperature geothermal field of Nesjavellir. Determination of optimal pH of deaerated freshwater and effective control of the scaling in the Sudurnes District Heating system has also been made possible by this study.

1. INTRODUCTION

Magnesium-silicate scaling in Icelandic district heating systems was first encountered in Hveragerði. There, high temperature geothermal water and fresh water were mixed followed by deaeration. This resulted in heavy scaling in the district heating system. The scaling mineral was magnesium-silicate and aluminum-silicate. To solve this problem the fresh water was heated with steam only. This reduced the scaling to a manageable level, but regular chemical cleaning of the pipelines had to be done in several streets (Þórhallsson *et al.* 1975).

Magnesium-silicate scaling has also occurred in two other Icelandic district heating systems where geothermal steam was used for heating magnesium-rich fresh water in heat exchangers. This was in the Hitaveita Reykjahlíðar (Reykjahlíð District Heating) in Námafjall geothermal area and Hitaveita Suburnesja (Sudurnes District Heating) in the Svartsengi geothermal area.

The magnesium-silicate scaling has been extensively studied in Iceland both theoretically and experimentally (Kristmannsdóttir *et al.*, 1983).

In 1990 the Hitaveita Reykjavíkur (Reykjavik District Heating) began utilizing the heat from a nearby high temperature geothermal field, Nesjavellir. Previously, the company had only used low temperature waters from the geothermal fields in Reykjavik and

Mosfellsbær for a system that serves 140,000 inhabitants of the capital city and nearby towns.

Pilot plant experiments had indicated that some mixing of the deaerated freshwater and geothermal water could be tolerated if the mixing ratio was carefully controlled (Gunnlaugsson and Einarsson, 1989).

After introducing the water from Nesjavellir, the deaerated water was allowed to mix with the geothermal water, but control of the mixing ratio was insufficient and heavy scaling occurred in the pipeline system. It soon became evident that scaling was more severe than expected and an elaborate study of the problem was initiated immediately to determine whether it would be possible to mix the two types of waters without scaling. The studies consisted of three types of tests: experiments in plastic containers, mixing experiments in specially developed incubators and scaling studies in experimental grids with different mixing ratios and flowing conditions (Hauksson *et al.*, 1992). The results of experiments soon led to the abandonment of any mixing and the distribution system had to be modified slightly to keep the waters separated at all times.

In 1991 Hitaveita Suburnesja installed several Ormat turbines which use the surplus steam at atmospheric pressure, from the power plant in Svartsengi, for electrical production. Fresh water is heated in the Ormat condensers from 5 °C to 25 °C. The higher inlet temperature of fresh water to the heating plant caused less condensation of low pressure steam in the direct contact heat exchangers. The process water thus had higher pH in subsequent heating steps. The small pH increase from 8.9 to 9.3 resulted in increased magnesium-silicate scaling. By using the results from the experiments performed by Hitaveita Reykjavíkur it could be shown that this small pH increase was sufficient to make the water supersaturated and cause the increased scaling (Hauksson, 1991).

A joint project was then initiated combining the force of Orkustofnun, Kemia sf, Hitaveita Reykjavíkur and Hitaveita Suburnesja in order to conduct the incubator study and to determine the solubility and scaling rate of magnesium-silicate in the temperature range 60 °C to 120 °C. The results of these experiments were then used for determining optimal process pH for the heated fresh water of both the Nesjavellir plant and the Svartsengi plant (Hauksson and Þórhallsson, 1993).

This paper deals with these experimental studies.

2. EXPERIMENTAL

Scale formation was first tested by storing experimental mixtures in plastic containers in a water bath and filtering the solids formed after several days for analysis by both wet chemistry and X-ray diffraction.

The precipitation rate experiments were done in an incubator with forced circulation. The incubator was in a constant temperature bath. The temperature of the bath was controlled by a PID regulator to a tenth of a degree. The water in the incubator was pumped through a narrow pipe to enhance the turbulence and the contact of the fluid and the incubator walls. The incubator was made of stainless steel and enclosed in electrically-heated oil.

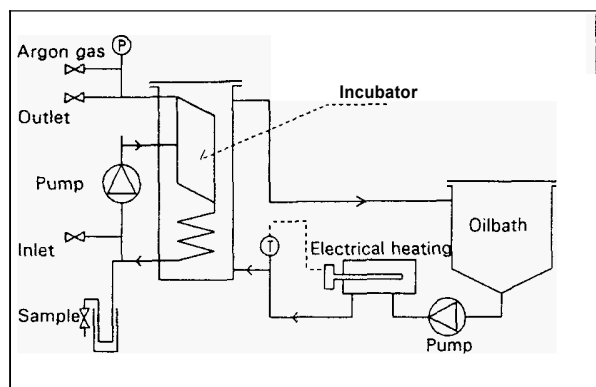


Figure 1 Incubator with forced circulation, in oil bath.

Before each experiment the incubator was rinsed well by allowing the water to flow through it for few days. The first sample was taken and the incubator was closed. The incubator was then pressurized by Argon gas and samples were withdrawn at regular intervals for analysis.

By filtering the samples and analysing the concentration of magnesium and silica in the filtrate, the amount of precipitated magnesium-silicate could be determined.

The sample was filtered through a $0.2\ \mu\text{m}$ membrane filter and the filtrate acidified by HNO_3 for the analysis of Na, K, Mg, Ca by ICP and AAS and SiO_2 by colorimetry. A small portion was also withdrawn for measuring pH after cooling the sample to 25°C . Each experiment lasted for up to four days.

Finally, scaling tests were made in a grid with controlled flow rate. For measurement of scaling rate, small coupons made of stainless steel were inserted into the water and withdrawn after few weeks for weighing and chemical analysis of the scale.

3. RESULTS OF EXPERIMENTS

3.1 Mixing experiments

In Reykjavik, the experiments were done for mixtures of low temperature geothermal water from the Reykjavik district heating system and heated fresh water from Nesjavellir plant. These experiments were done at 60 , 83 and 93°C . Typical chemical analysis of the tested waters is shown in Table 1.

Table 1. Typical analysis of tested waters.

	Reykjavik	Nesjavellir	Svartsengi
pH/ 25°C	9.6	8.5	9.3
CO_2	26.0	36.3	11.6
H_2S	1.0	0.2	0.1
SiO_2	86.3	21.1	12.9
Na	47.3	10.2	33.3
K	1.0	1.2	1.5
Ca	2.3	9.0	7.8
Mg	0.03	5.1	6.7
SO_4	19.2	10.6	10.0
Cl	12.7	7.8	74.0

Concentrations in mg/kg.

The mixing of geothermal water and heated fresh water resulted

in the formation of solid particles, which deposited on the incubator walls, or could be separated from the water by filtration.

First, different mixtures were stored in plastic bottles in a hot water bath for 7 days. Then 3 liters of the mixture were filtered to obtain a sufficient amount of precipitate for weighing and quantitative analysis. Analysis and examination by electron microscopy showed the filtered solid to be amorphous magnesium-silicate.

To better simulate actual conditions in narrow pipelines, further studies were done in forced circulation incubators. Figure 2 shows examples of the rate of concentration change for magnesium in the filtrate at different mixing ratios. The precipitation rate was high initially but after 3 to 4 days, it had slowed down considerably and reached a virtual equilibrium. At the same time the silica content decreased and also the pH. Concentration of other constituents did not change significantly.

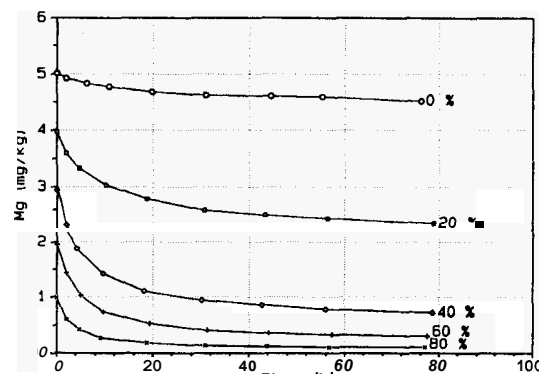


Figure 2 Concentration of magnesium versus time.

The retention time in the district heating system is normally less than a day and therefore the initial precipitation rate is of most interest. After 3 days when the reaction had reached a virtual equilibrium, the concentration continued to decrease at a slow rate. This is believed to be caused by annealing and uptake of magnesium ions into the already formed amorphous material on the incubator walls, which eventually would result in the formation of crystalline magnesium-silicate mineral. This reaction is too slow to be of practical significance for the study of the magnesium-silicate scaling in district heating systems.

Figure 3 shows example of the concentration change of magnesium in the filtrate, for different mixing ratios, after approximately 3 days incubation time.

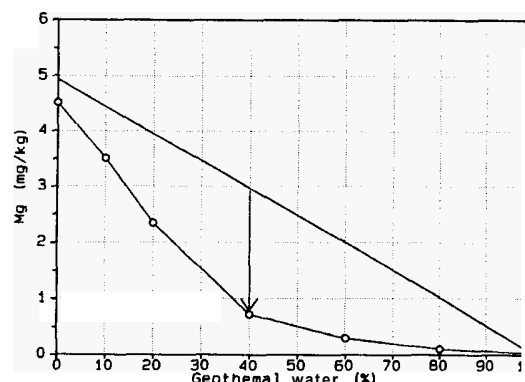


Figure 3 Concentration of magnesium versus mixing ratio of geothermal water and fresh water.

The greatest concentration decrease occurred at 40 % ratio of geothermal water in fresh water where 13 mg of amorphous magnesium-silicate precipitated from each liter of water. No change in concentration was observed in pure geothermal water, but in pure deaerated fresh water, the magnesium content decreased slightly indicating supersaturation in the water.

3.2 Effect of pH and temperature

In Svartsengi, the process water was studied at different pH and at higher temperatures. The pH was changed by injecting a small stream of geothermal steam, containing CO₂ and H₂S, into the heated and deaerated water. These experiments were done at 80 °C, 100 °C and 120 °C. Typical analysis of tested water is shown in Table 1.

First, the precipitation rate was studied in the deaerated process-water without any pH adjustments but at different temperatures. Figure 4 shows the concentration changes of magnesium in these experiments.

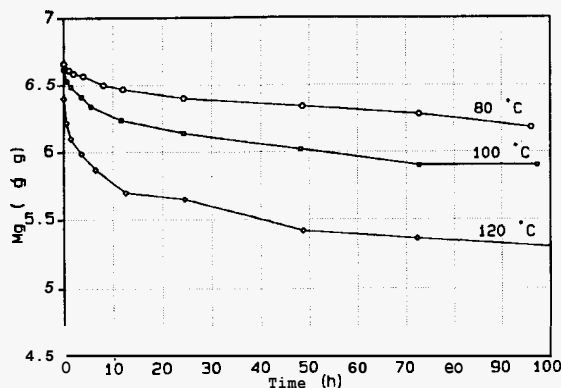


Figure 4 Concentration of Mg versus time, without pH control.

The precipitation rate was faster and more magnesium-silicate precipitated at higher temperatures than at lower temperatures. At 80 °C the concentration change in four days amounted to the precipitation of 1.8 mg of magnesium-silicate per liter of water, at 100 °C 3.1 mg precipitated and at 120 °C, 4.4 mg.

The pH was then lowered by injection of geothermal steam into the deaerated water. Figure 5 shows the effect of pH adjustment on the concentration of magnesium.

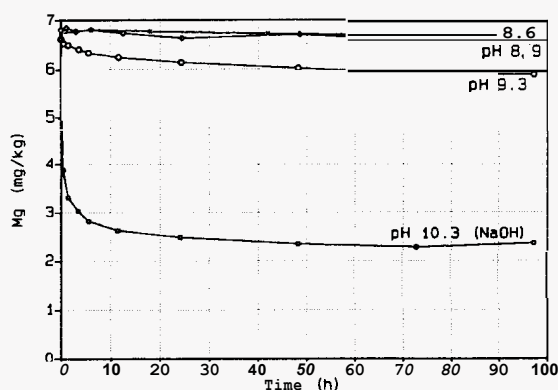


Figure 5 Concentration of Mg versus time, at 100 °C.

The effect of pH is evident. In deaerated water without steam injection 3.1 mg of magnesium-silicate precipitated per liter of water. When the pH was lowered below pH 8.9 no magnesium-silicate precipitated, but when NaOH was added the concentration decreased very rapidly.

3.3 Scaling tests

The scaling tests in experimental grids showed the scaling rate to be dependent on flow rate and turbulence. Much greater scaling rates were obtained at higher turbulence.

Typical wet chemical analysis of the scale is shown in Table 2. The Mg:Si ratio varied and was on the average around 1.0 in the Reykjavik experiments. In Svartsengi the Mg:Si ratio was around 1.3, presumably reflecting higher Mg:Si ratio of dissolved ions in the Svartsengi waters than in the water mixtures in Reykjavik.

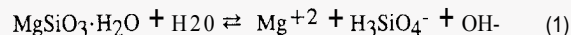
Table 2. Analysis of magnesium-silicate scale.

	Reykjavik	Svartsengi
CaO %	0.6	0.2
MgO %	26.5	35.9
SiO ₂ %	39.6	41.7
Sum %	66.7	77.8

4. DISCUSSION

4.1 Solubility of Magnesium-Silicate

The solubility of magnesium-silicate can be described by the following equilibrium:



and the solubility constant at equilibrium is:

$$K_{\text{sp}} = (\text{Mg}^{+2})(\text{H}_3\text{SiO}_4^-)(\text{OH}^-) \quad (2)$$

From chemical analysis of the process water the ion product can be calculated:

$$Q = (\text{Mg}^{+2})(\text{H}_3\text{SiO}_4^-)(\text{OH}^-) \quad (3)$$

If the ion-product (Q) is higher than the solubility constant (K_{sp}), then the water is supersaturated and precipitation of magnesium-silicate will occur.

In Figure 6 the ion-product is shown for the experiments. The open circles show the ion-product in the initial sample, and the solid circles show the ion-product after 3-4 days incubation.

The calculation is based on the activities of the ions, accounting for effect of ion strength and complex formation of relevant ions in the water. This was done by a computer program VDATA developed for studying geothermal process water (Hauksson, 1993). In this program the same equilibrium constants for complex formation are used as in the widely used WATCH program (Arnórsson *et al.*, 1982).

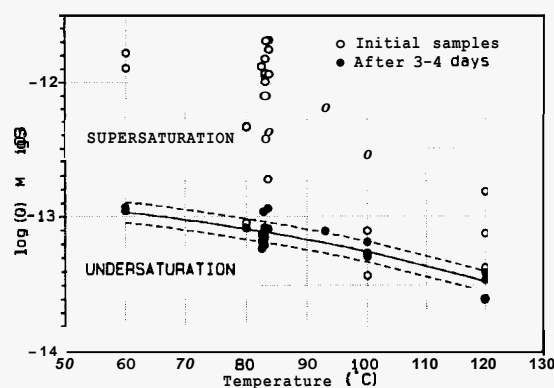


Figure 6 Ion-product, log(Q), versus temperature

Initially, the ion-product is higher than the solubility constant and the water is thus supersaturated. After few days, magnesium-silicate has precipitated and the water has reached equilibrium.

A best fit for the equilibrium points was calculated and is shown by the following equation.

$$\log(K_{\text{sp}}) = -12.90 + 0.00262 T - 6.212\text{E-}05 T^2 \quad (4)$$

K_{sp}: Solubility constant (mol/l)³
T: Temperature (°C)

The solid line shows the correlation and the broken lines the standard deviation.

4.2 Precipitation rate

The retention time for the water in the district heating system is less than a day and therefore the initial precipitation rate is of practical interest.

By plotting the rate of precipitation vs. ratio of the ion-product and the solubility constant a straight relationship was obtained (Figure 7). The linear relationship was better in the mixing experiments at 60 °C and 83 °C possibly because of greater concentration changes, and therefore, better determination accuracy. These experiments showed the activation energy for the precipitation reaction to be approximately 50 kJ/mol.

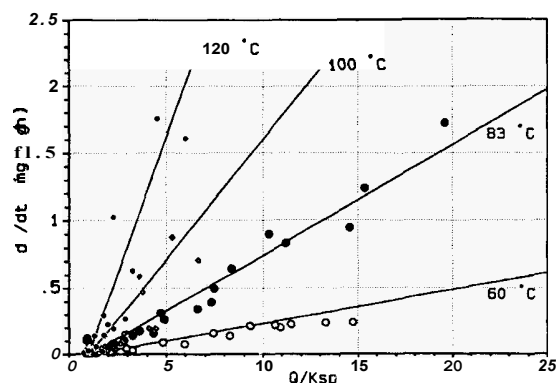


Figure 7 Precipitation rate versus supersaturation.

The following equation describes the precipitation rate as a function of temperature and supersaturation.

$$dw/dt = A \exp(-E/RT) (Q/K_{sp}-1) \quad (5)$$

dw/dt : scaling rate (mg/kg/h)
 A: rate constant 1.8×10^6 (mg/kg/h)
 E: activation energy 50000 (J/mol)
 R: gas constant 8.314 (J/K/mol)
 T: temperature (K)
 Q: ion-product (mol/l)³
 K_{sp} : solubility constant (mol/l)³

The solid lines in Figure 7 were drawn according to the above equation for experimental temperatures of 60, 83, 100 and 120 °C.

This equation is to be used primarily for predicting scaling rates in turbulent flow similar to the conditions in the experiments.

4.3 Actual scaling rate

The mixing of geothermal and heated fresh waters by the Reykjavik district heating company was abandoned after 10 months operation. During this time sufficient scale had collected in the 4 km pipelines, from the mixing point to the Reykjavik district system, to seriously affect their performance. After the operation period the pipelines were cleaned mechanically with cleaning pigs.

The scale in the pipeline was estimated both by measuring scale thickness and density at various places and also by weighing the collected scale during cleaning operations (Gislason, 1991).

During this period the mixing ratio and temperature were monitored and chemical samples collected. By calculating the supersaturation by equation (4) and scaling rate by equation (5) the amount of scale in the pipeline could thus be predicted at each time. This enabled the comparison of predicted scale formation by the above method and actual scale that had collected in the pipeline. The results are shown in Table 3.

Table 3. Comparison of predicted and actual scale

Method	Amount (kg)
Chemical prediction	17,000
Thickness measurement	10,000
Cleaning operation	13,000

The predicted scale is slightly greater than actual scale, possibly because part of the precipitate does not form a scale on the pipe walls and is swept away with the flowing stream as suspended matter.

5. CONCLUSIONS

Mixing of deaerated fresh water and geothermal water will cause amorphous magnesium-silicate scaling if the pH is not regulated.

The solubility is controlled by the concentration of magnesium, silica, pH and temperature. The solubility constant for amorphous magnesium-silicate, was determined experimentally, and it can be used for calculation of supersaturation in processed water at different temperatures, pH and chemical concentrations.

These results have been applied at the power plants in Svartsengi and Nesjavellir where optimal pH for the deaerated water was calculated and adjusted by mixing live steam, containing CO₂ and H₂S, with the water. The results are encouraging as scaling in the water is now a minor problem.

6. ACKNOWLEDGEMENTS

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