Presented at “Short Course on Geothermal Development and Geothermal Wells”,
organized by UNU-GTP and LaGeo, in Santa Tecla, El Salvador, March 11-17, 2012.

UNITED NATIONS
UNIVERSITY
GEOTHERMAL TRAINING PROGRAMME

LaGeo S.A. de C.V.

# SCALING PREDICTION MODELLING

**Einar Gunnlaugsson**,
Orkuveita Reykjavíkur
Reykjavík
ICELAND
*einar.gunnlaugsson@or.is*

## ABSTRACT

Scaling problems are often associated with the utilization of geothermal fluid. In general water chemistry is dependent on water rock interaction and is controlled by mineral equilibrium. Knowledge of the processes causing scaling, the solubility of the forming minerals and the water chemistry makes it possible to predict scaling during geothermal utilization. The most common scaling products are calcium carbonate and amorphous silica which both can be predicted fairly well from chemical analysis of the water.

## 1. INTRODUCTION

Chemical problems often rise during utilization of geothermal water. These problems can be scaling where formation of solids are in drillholes and surface installation, corrosion of metals in casings in drillholes or other installations and pollution due to gas and liquid discharge from geothermal power plants. The most common deposits in geothermal utilization are due to silica, iron oxides, iron silicates, sulphides, calcite and magnesium silicates.

Formation of solid material in wells, piping systems and during reinjection is most common. Knowledge of the physical and chemical conditions causing mineral deposition from geothermal water allows an evaluation of the magnitude of the scaling problems and may aid in visualizing how they could be overcome. During exploitation cooling, heating, degassing or boiling, dissolution of materials from pipes and mixing of inflow from two or more aquifers, each with its characteristic temperature and chemistry can lead to scaling. By comparing the water chemical composition with the solubility of the minerals it is possible to predict scaling. It should be kept in mind that this study does not tell anything about the deposition rate.

## 2. MINERAL EQUILIBRIA

The composition of geothermal fluid is controlled by a temperature dependent reaction between the geothermal fluid and minerals. The formation of hydrothermal minerals is affected by temperature, pressure, rock type, permeability, fluid composition and duration of activity (Brown 1978). At temperatures above 280°C the type of rock is insignificant but at lower temperature it is most pronounced. Chemical equations for formation of alteration minerals can be written to which the water composition is compared. The approach to chemical equilibrium for natural water-rock systems can be tested by comparing the water composition to theoretical composition of alteration minerals using thermodynamic data (Helgeson 1969, Helgeson et al. 1969, Robie et al. 1978).

Fluid composition in many geothermal fields worldwide appear to closely approach chemical equilibrium with secondary minerals for all major aqueous components except Cl and B (Giggenbach, 1980; 1981). For Icelandic waters the equilibrium has been presented by temperature dependent graphs of cation/proton ratios and concentration of dissociated weak acids from geothermal well discharges (Arnórsson et al., 1983). Examples of these graphs are shown in Figure 1. Chemical geothermometers are based on chemical equilibrium. The equations used are either obtained directly from thermodynamic data of known chemical reactions or as empirical relations.

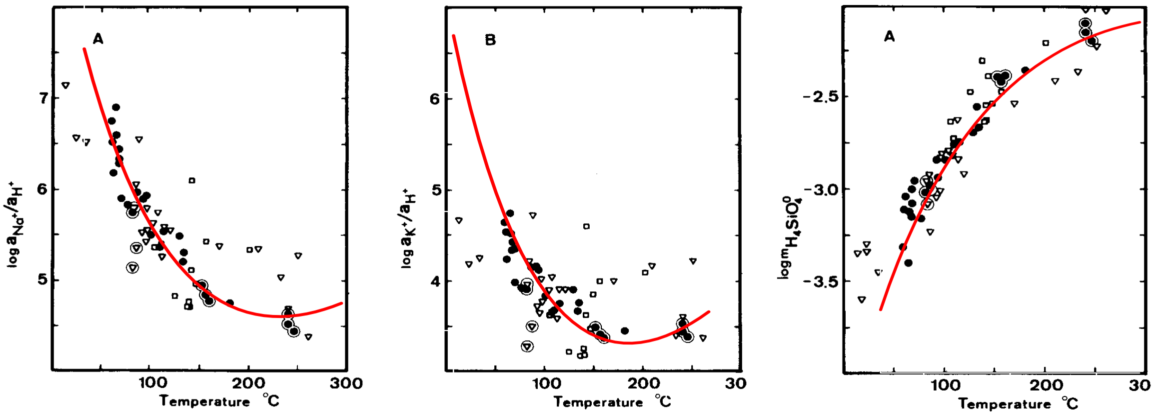

FIGURE 1: Examples of cation/proton activity ratios and undissociated acid concentrations in Icelandic geothermal waters

## 3. SCALING PREDICTION

Prediction of scaling is based on comparison of water chemistry to the stability of minerals and deviation from equilibrium conditions. The chemical composition of the water is usually expressed as total concentration of the elements. The reactions describing solubility of minerals are based on activity of chemical species. For the comparison the activity of the chemical species have to be calculated from the chemical composition. Various computer programs have been written to deal with these calculations such as the WATEQ-series (Truesdell and Jones, 1974, Plummer et al. 1976), SOLMNEQ (Kharaka and Barnes 1973) and WATCH (Arnórsson et al. 1982) and later versions of these programs.

Here the WATCH program is used for these calculations. The concentrations of the species considered in the program are expressed in terms of the component concentrations by mass balance equations, and the chemical equilibria between the species are expressed as mass action equations. The program contains provisions for 67 different aqueous species, in addition to $H^+$ and $OH^-$. The calculations are done at a selected temperature. The output from the program lists the component and species concentrations at the reference temperature, as well as the activity coefficients. Ionic balance, geothermometers temperatures, partial pressures of gases, and redox potentials are also output. Finally, the ion activity products and solubility products of selected minerals are computed. From these, the corresponding saturation indices can be trivially obtained. The WATCH program can also be used to compute the resulting species concentrations, activity coefficients, and activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in the study of scaling.

Scaling prediction depends on the quality of the chemical analysis. The pH is the most critical parameter for the interpretation of the composition of natural waters since hydrogen ($H^+$) participates in almost all chemical reactions. pH is very sensitive to errors and mistakes made during sampling and analysis can greatly affect the calculated result.

## 4. CALCITE SCALING

Calcite is the most common scaling product. The solubility of calcite as function of temperature is shown in Figure 2. The solubility increases with decreasing temperature. Therefore cooling of geothermal water does not cause scaling of calcite. Calcite scaling is on the other hand associated with boiling and mixing of inflow from two or more aquifers, each with different chemistry and temperature.

The solubility of calcite can be described by the following reaction:

$$CaCO_3 = Ca^{++} + CO_3^{--} \qquad (1)$$

calcite = calcium + carbonate

The equilibrium constant for the reaction is:

$$K_{calcite} = a_{Ca++} \bullet a_{CO3--} \qquad (2)$$

From the chemical composition the activity of the chemical species and the solubility product for calcite can be calculated.

$$Q_{calcite} = a_{Ca++} \bullet a_{CO3--} \qquad (3)$$

If the solubility product Q is higher than the equilibrium constant for selected temperature the water is supersaturated and calcite can deposit. Experience shows that supersaturation in order of about 0.5 have to be reached before deposition forms.

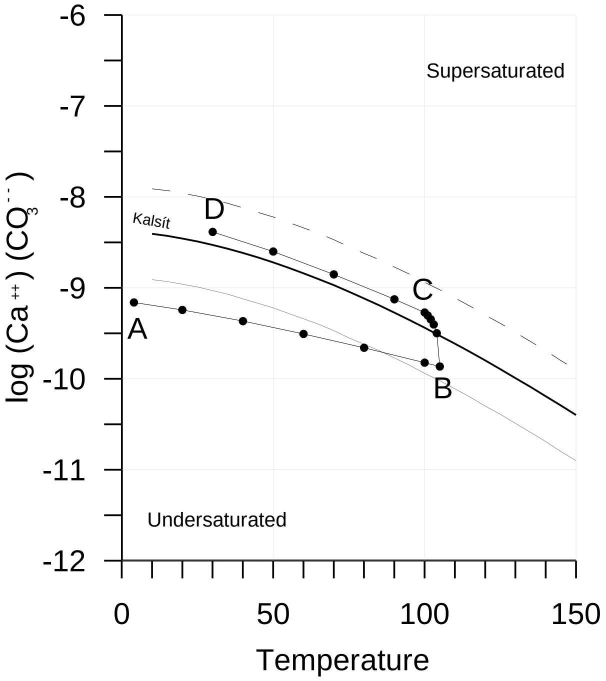

FIGURE 2: Solubility of calcite. The solid line represents the solubility and the dashed lines the division of error for the solubility

To envisage the effects of boiling of geothermal water upon the stage of calcite saturation it is convenient to express the calcite dissolution as:

$$CaCO_{3,calcite} + 2H^+ = Ca^{++} + CO_{2,aq} + H_2O \qquad (4)$$

The equilibrium constant for reaction (4) is given by:

$$K_{calcite} = a_{Ca++} / a^2_{H+} \bullet a_{CO2,aq} \qquad (5)$$

The equilibrium constant for the first dissociation constant of carbonic acid (aqueous carbon dioxide, i.e. $CO_{2,aq}$ is equivalent to $H_2CO_3$) is given by:

$$K_{H2CO3} = a_{H+} \bullet a_{HCO3-} / a_{H2CO3} \qquad (6)$$

The second dissociation constant is then:

$$K_{HCO3-} = a_{H+} \bullet a_{CO3--} / a_{HCO3-} \qquad (7)$$

From the equitation it can be seen that the activity of hydrogen ($H^+$) and therefore the pH affect the calcite equilibria. Boiling or degassing of water increases the solubility product for calcite which can increase to supersaturation of that mineral.

Figure 2 also shows the effect of heating, boiling and cooling of geothermal water with regard to the saturation of calcite. Point A represents cold water composition and the dashed line to point B represents heating of that water to 105°C. It is assumed that the water is degassed with boiling from 105°C to 100°C, point C. The solubility product changes significantly during boiling and the water which was undersaturated becomes slightly supersaturated. The curve from the point C to the point D shows cooling of the water to 30°C. Calcite scaling associated with boiling is always by far the strongest at the first level of boiling. The magnitude of calcite supersaturation caused by boiling depends on the salinity of the water and its temperature.

Mixing of inflow from two or more aquifers, each with a different chemistry and temperature often affects the solubility product of calcite towards supersaturation. Equilibrium is reached again by precipitating calcite. Calcite depositions can be found immediately after mixing such as in deep well pumps. Dissolution of calcium from asbestos pipelines can increase the solubility product of calcite which may cause supersaturation and formation of calcite depositions.

## 5. SILICA SCAILING

The silica concentration in geothermal systems is controlled by the solubility of quartz and chalcedony (Fournier and Rowe, 1966; Mahon, 1966) and increases with increasing temperature (Figure 3). During cooling the silica is in solution until solubility of amorphous silica is reached. At still lower temperature the water becomes supersaturated and silica depositions can be expected.

The figure shows that water in equilibrium with rock in low temperature areas up to about 130°C can be cooled down to 30°C without deposition of silica. Water in equilibrium with rock at 220°C reaches amorphous silica saturation if cooled down to about 90-100°C. During boiling, the concentration of silica concentration increases due to steam loss. When amorphous silica saturation curve is reached precipitation of silica begins.

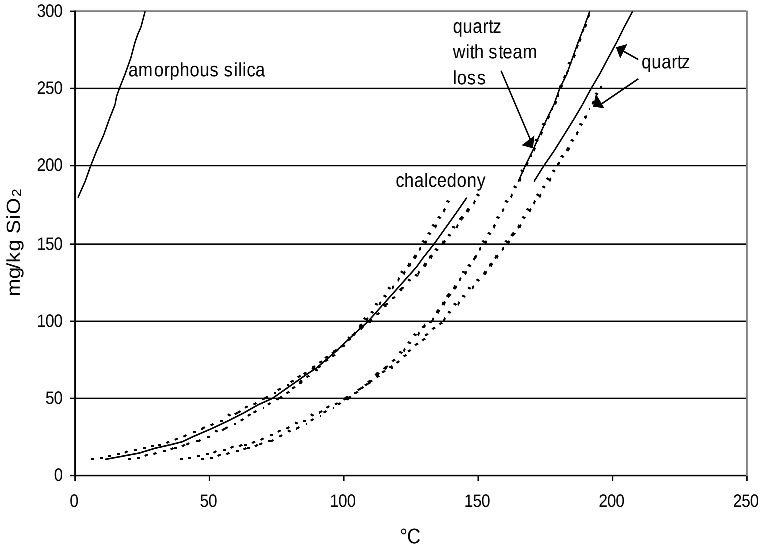

FIGURE 3: Solubility of quartz, chalcedony and amorphous silica as a function of temperature. The silica concentration is that of undissociated silica.

## 6. MAGNESIUM SILICATE

Depositions of magnesium silicate can form where fresh groundwater is mixed with geothermal water. Experiments in order to determine the solubility of magnesium silicate under these conditions are described by Hauksson et al., 1995. The solubility of magnesium silicate can be described by the following reaction:

$$MgSiO_3 \bullet H_2O + H_2O = Mg^{++} + H_3SiO_4^- + OH^- \qquad (8)$$

The equilibrium constant for reaction (8) is given by

$$K_{\text{Mg-silicate}} = a_{Mg^{++}} \bullet a_{H3SiO4-} \bullet a_{OH-} \qquad (9)$$

Figure 4 shows the solubility of magnesium silicate as a function of temperature in range of 60-120°C. The reaction shows that the solubility depends on the activity of magnesium, silica and hydroxide (pH) as well temperature.

The calculated solubility product (Q) for these species in the water sample can be compared with the equilibrium constant similar as for calcite.

$$Q_{\text{Mg-silicate}} = a_{Mg^{++}} \bullet a_{H3SiO4-} \bullet a_{OH-} \qquad (10)$$

If the solubility product (Q) for magnesium silicate is higher than the equilibrium constant for a selected temperature the water is supersaturated and magnesium-silicate can deposit.

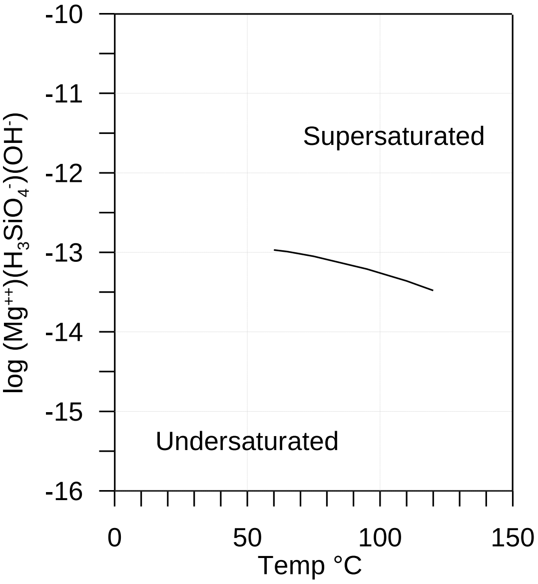

FIGURE 4: Solubility of magnesium silicate as a function of temperature

Cold fresh groundwater always contains some magnesium but the concentration of silica is relatively low. Degassing of water by boiling increases the pH of the water. These changes could lead to supersaturation of magnesium silicate. The content of magnesium in geothermal water is usually very low and the water calculates to be undersaturated with respect to magnesium-silicate. The content of silica is on the other hand higher than in cold fresh water and the content increases with increasing temperature. Mixing of cold fresh water and geothermal water may therefore cause deposition of magnesium silicate.

## REFERENCES

Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H., 1983: The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta, 47,* 547-566.

Fournier, R.O., and Rowe, J.J., 1966: Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Am. J. Sci., 264,* 685-697.

Giggenbach, W.F., 1980: Geothermal gas equilibria. *Geochim. Cosmochim. Acta, 44*, 2021- 2032.

Giggenbach, W.F., 1981: Geothermal mineral equilibria. *Geochim. Cosmochim. Acta, 45*, 393-410.

Helgeson, H.C., 1969: Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci., 267,* 729-804.

Helgeson, H.C., Brown, T.H., and Leeper, R.H., 1969: Handbook of theoretical activity diagrams depicting chemical equilibria in geothermal systems involving an aqueous phase at one atm. and 0° to 300°C. *Cooper, San Francisco,* 253 pp.

Mahon, W.A.J., 1966: Silica in hot water discharged from drillholes at Wairakei, New Zealand. *New Zealand Jour. Sci., 9*, 135-144.

Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1978: Thermodynamic properties of minerals and related substances at 298.15 °K and one bar pressure at higher temperatures. *U.S. Geological Survey Bull., 1452,* 456 pp.