

## IMPORTANCE OF CHEMISTRY IN GEOTHERMAL EXPLORATION AND UTILIZATION

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### ABSTRACT

Chemistry of geothermal water plays an important role in geothermal exploration, drilling and monitoring of geothermal resources. In the exploration it is used to predict underground temperature and origin of water. It also defines the environmental effect of disposal of the water. The chemistry is often the key parameter to distinguishing and solving problems occurring during utilization. Through mineral equilibria scaling can be predicted and the chemistry identifies the possibility of corrosion. Special emphasis is on the quality of data and how that affects the interpretation.

### 1. INTRODUCTION

The chemistry of geothermal fluid is an important factor in exploration, development and utilization of geothermal resources. In the exploration phase geochemistry is used to evaluate the origin of the water, to estimate underground temperature, characterize the reservoir chemistry in respect to utilization and to define environmental impact of the utilization. The process of exploring, developing and utilization of geothermal resources can be divided into three main phases, (a) surface exploration, (b) exploratory and production drilling, and (c) utilization (Table 1).

TABLE 1: Main tasks of water chemistry in geothermal exploration, drilling and utilization

<b>Surface exploration</b>
Evaluate origin of water Estimate underground temperature Cold water composition Map the extent of the geothermal system Characterize the reservoir chemistry with respect to utilization Define environmental impact with respect to utilization
<b>Drilling</b>
Assess water composition with reference to utilization Establish changes in total well discharge composition during long term testing Provide chemical data for construction design Define scaling and corrosion problems Methods for disposal of geothermal water
<b>Utilization</b>
Monitor chemical changes Monitor chemical parameters of the fluid in the distribution system Participate in solving problems arising from utilization

The water chemistry is relevant for all the phases and the geochemist participates in all the phases involved in research and utilization. The geochemist together with other geothermal specialists delineate model of the geothermal system which has to be revised as more data is collected. Similarly the geochemist always has to revise the previous data when new data is collected. The geochemical methods used for interpreting the water chemistry are the same through all the phases. This information is important for evaluation and recalibration of reservoir simulation models used for predicting the production of the reservoir.

## 2. RELIABILITY OF DATA FOR INTERPERTATION

A geochemical study of geothermal fluids essentially involves three main steps. These are:

- Collection of samples
- Chemical analyses
- Interpretation of the data

Collection of samples requires a good understanding of chemical analysis and interpretation. It involves some measurements on-site and appropriate treatment of the sample. During storage the chemical composition of the sample may change, at least with respect to some components. The analysis in the laboratory is usually done according to some well described and tested methods. Analysis in the laboratory, no matter how well done, will not give correct information on the chemical composition of the water at the sampling site if collection and sample treatment is not inadequate. Interpretation of the analytical data suffers if collection of sample or analysis is unsatisfactory.

In this paper introduction to collection of low-enthalpy geothermal water and geochemical interpretation is given and some examples where exploitation affects equilibrium and even in some cases cause scaling.

Only the collection of low-temperature geothermal water will be discussed here. The same methods should be used for collection of samples of groundwater. The collection of water and steam is much more complicated and is not an issue of this course.

The collection of water is a routine procedure and should be described similar to analytical methods in a laboratory. The main components that are generally analysed for low-temperature water during geochemical exploration, well testing and monitoring studies are listed in table 2. Beside these component samples for isotopic determination may be collected as well as for various trace elements.

TABLE 2: Main chemical components analysed in low-temperature geothermal water

Kations	Anions	Volatiles	Other
Sodium (Na)	Sulphate (SO <sub>4</sub> )	Hydrogen (pH)	Silica (SiO <sub>2</sub> )
Potassium (K)	Chloride (Cl)	Total carbonate (CO <sub>2</sub> )	Boron (B)
Calcium (Ca)	Fluoride (F)	Hydrogen sulphide (H <sub>2</sub> S)	Conductivity
Magnesium (Mg)		Dissolved oxygen (O <sub>2</sub> )	Dissolved solids
Iron (Fe)			
Aluminium (Al)			

When the sampling point has been selected it should be described and on-site measurements carried out. It includes measurement of temperature, flow rate and geographical co-ordinates for the sampling site. Some determinations are best done in the field such as dissolved oxygen (O<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S). Sometimes pH and total carbonate is also determined on-site.

During collection the sample has to be cooled, especially for the volatile components. If pH, total carbonate and hydrogen sulphide is going to be analysed in a laboratory, the sample has to be cooled and stored in air-tight bottles. Commonly samples for determination of volatile components are kept in plastic bottles without previous cooling. The bottles are then taken to laboratories and in spite of accurate analyses of the water in the bottle, the result does not represent the spring or the well. During storage the volatiles degas and the recorded values cannot be used in a detailed evaluation of the sample. It should be kept in mind that accurate determination of the pH is essential for all further calculations since it participates in almost all chemical reactions. Calcite scaling prediction is highly based on the measured pH. An inaccurate pH-value may therefore lead to a wrong prediction.

The sample collected for determination of cations has to be filtrated and acidified to avoid precipitation. Usually samples for determination of sulphate can be collected without any treatment. But in the case of high concentration of hydrogen sulphide (H<sub>2</sub>S) it may oxidize which then increases the concentration of sulphate. In that case hydrogen sulphide (H<sub>2</sub>S) has to be precipitated for example by adding zinkacetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>).

### 3. MINERAL EQUILIBRIA

The composition of geothermal fluid is controlled by temperature dependent reactions 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 temperatures it is most pronounced.

Chemical equations for formation of alteration minerals can be written to which the water composition is compared. For example at equilibrium, ratios of sodium and potassium in a solution are controlled by a temperature dependent exchange reaction:



and the equilibrium constant for the reaction is written as:

$$K_{\text{eq}} = [\text{Na}^+]/[\text{K}^+] \quad (2)$$

Activity of the given species is shown in brackets and the activity of the solid phase is assumed to be unity. 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 and activity phase diagrams (Bowers et al. 1984).

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, Arnórsson et al., 1983, Michard, 1991). Figures 1 and 2 are examples of graphs which can be used to demonstrate equilibrium between water and minerals (Arnórsson et al., 1983). Figure 1 describes the temperature dependence of the cation/proton ratios and figure 2 the concentration of dissociated weak acids. The equations describing the temperature dependence of the cation/proton ratios and undissociated weak acid concentrations are listed in Table 3.

Prior to exploitation geothermal water may be in equilibrium with the alteration minerals. Mixing with cooler groundwater may cause deviation from equilibrium and that has to be studied by interpretation of the monitoring data.

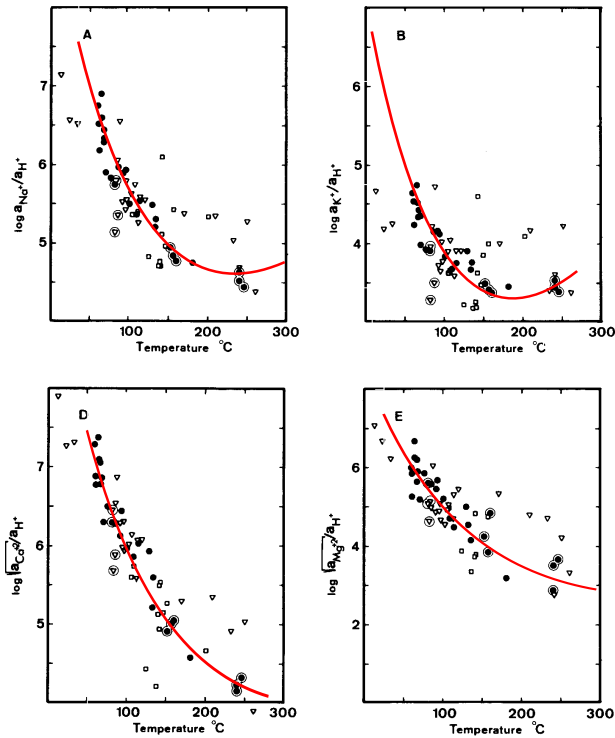


FIGURE 1: The temperature dependence of some cation/proton activity ratios in geothermal water in Iceland

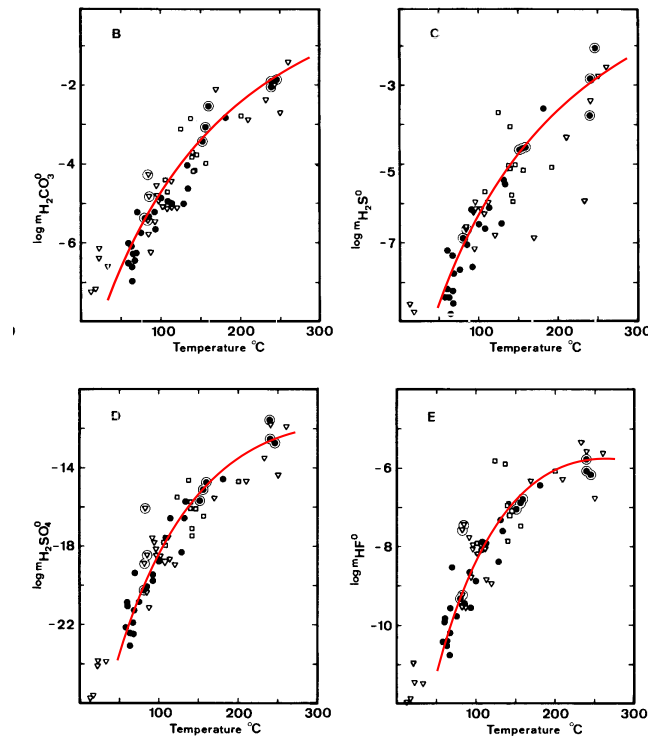


FIGURE 2: The temperature dependence of some undissociated acid concentration in geothermal water in Iceland

TABLE 3: Equations describing the temperature dependence of cation/proton ratios and undissociated weak acid concentrations in geothermal well discharges (Arnórsson et al. 1983).

Weak acid ion ratio moles/kg	Temperature function
$\log \text{H}_4\text{SiO}_4^0$	$-0.588 - 0.00441T - 1515.21/T + 1.3470 \log T$
$\log \text{H}_2\text{CO}_3^0$	$-1.794 - 0.00510T - 4469.63/T + 4.1414 \log T$
$\log \text{H}_2\text{S}^0$	$-1.678 - 0.00355T - 5071.05/T + 3.8889 \log T$
$\log \text{H}_2\text{SO}_4^0$	$-6.436 - 0.03906T - 13335.68/T + 14.7958 \log T$
$\log \text{HF}^0$	$-5.262 - 0.03511T - 7964.11/T + 12.1022 \log T$
$\log \text{Na}^+/\text{H}^+$	$2.694 + 0.0223T + 4243.47/T - 6.2069 \log T$
$\log \text{K}^+/\text{H}^+$	$2.505 + 0.01971T + 3325.71/T - 5.7814 \log T$
$\log \sqrt{\text{Ca}^{+2}/\text{H}^+}$	$1.733 + 0.01117T + 3890.15/T - 3.9977 \log T$
$\log \sqrt{\text{Mg}^{+2}/\text{H}^+}$	$1.816 + 0.01078T + 3727.48/T - 4.1640 \log T$

The concentration and activity of the chemical species has 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.

#### 4. CHEMICAL GEOTHERMOMETERS

Chemical geothermometry refers to the use of chemistry to evaluate temperature in the geothermal reservoir. The chemical composition of the geothermal water is on a large extent controlled by chemical equilibria between water and minerals. Most of the major and minor elements dissolved in geothermal solutions are considered reactive components.

The most widely used chemical geothermometers for low-temperature water are the silica geothermometers and the cation geothermometers (Na-K and the Na-K-Ca geothermometers).

##### 4.1 Silica geothermometer

Dissolved silica is almost universally controlled by equilibrium with quartz in most geothermal systems with the exception of young basalt with geothermal systems at temperatures below  $\sim 180^\circ\text{C}$  in which the silica is controlled by the solubility of chalcedony, a metastable silica polymorph (Arnórsson, 1975, Arnórsson et al. 1982, Gíslason et al. 1997). With the aid of the solubility curves, the silica content of the water is related to temperature. It should be considered when applying the silica geothermometer that equilibrium between fluid and mineral only involves the unionized silica in solution. This is particularly significant for diluted waters with high pH.

In some groundwater the concentration of silica results from non-equilibrium reactions where silica is released to solution during acid alteration of silica minerals. Figure 3 shows the solubility curves of quartz, chalcedony as a function of temperature. Dilution of the geothermal water with cold or slightly heated unequilibrated groundwater affects the silica-geothermometer. If chemical equilibrium is attained after mixing the silica geothermometer will give the temperature of the last equilibrium after mixing. Low values will be obtained by the silica geothermometer if equilibrium is not attained. To deal with such water mixing models have been applied.

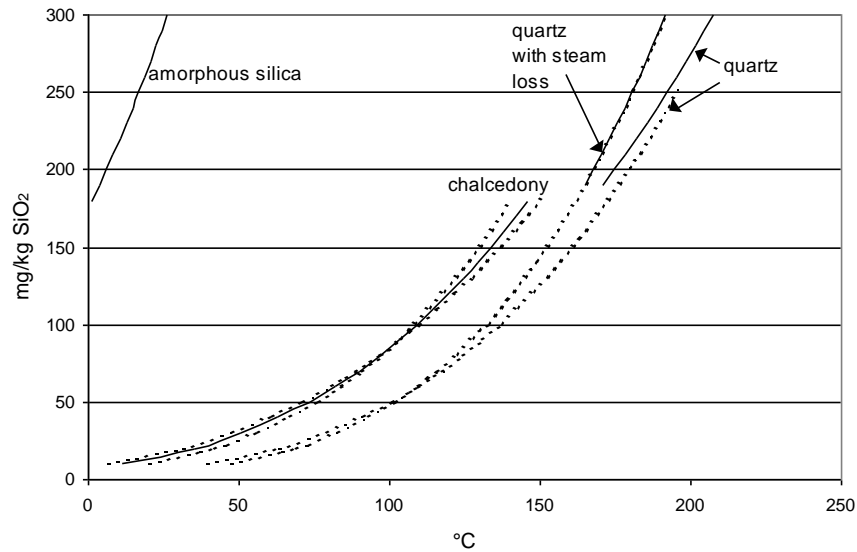


FIGURE 3: Solubility of quartz, chalcedony and amorphous silica as a function of temperature. The silica concentration is that of undissociated silica.

The solubility of amorphous silica is not used as geothermometer. It on the other hand it gives indications if silica scaling should be expected.

#### 4.2 Cation geothermometers

The Na-K geothermometer is based on temperature dependence of partitioning of sodium and potassium between the fluid and alkali feldspars. Figure 4 shows the Na/K ratio of waters in equilibrium with sodium and potassium feldspars. The main advantage of the Na/K geothermometer in geothermal exploration is that it is less affected by dilution and steam separation than other commonly used geothermometers. For the same reason the Na/K ratio is less affected by dilution caused by increased flow of cold groundwater due to exploitation.

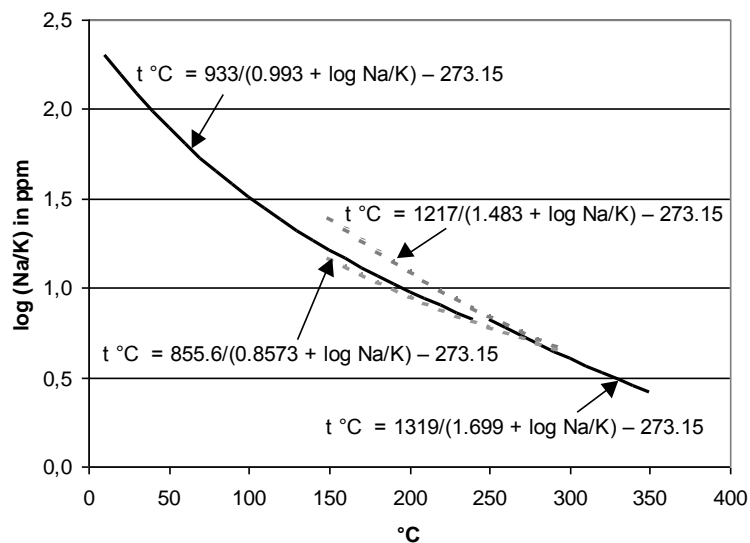


FIGURE 4: The temperature dependence of the concentration of Na/K

The Na-K-Ca geothermometer is an empirical correlation where all the main cations in feldspars are correlated to temperature.

Table 4 summarizes some commonly used equations as chemical geothermometers for geothermal water.

TABLE 4: Equations expressing the temperature dependence of selected chemical geothermometers using analytical concentrations (mg/kg).

<u>Chalcedony</u>			
$t\text{ }^{\circ}\text{C} = 1112/(4.91 - \log \text{SiO}_2) - 273.15$		25-180 °C	(a)
$t\text{ }^{\circ}\text{C} = 1264/(5.31 - \log \text{SiO}_2) - 273.15$	(after steam loss)	100-180 °C	(a)
$t\text{ }^{\circ}\text{C} = 1032/(4.69 - \log \text{SiO}_2) - 273.15$		25-180 °C	(b)
<u>Quartz</u>			
$t\text{ }^{\circ}\text{C} = 1164/(4.90 - \log \text{SiO}_2) - 273.15$		180-300 °C	(a)
$t\text{ }^{\circ}\text{C} = 1498/(5.70 - \log \text{SiO}_2) - 273.15$	(after steam loss)	180-300 °C	(a)
$t\text{ }^{\circ}\text{C} = 1309/(5.19 - \log \text{SiO}_2) - 273.15$		0-250 °C	(b)
$t\text{ }^{\circ}\text{C} = 1522/(5.75 - \log \text{SiO}_2) - 273.15$	(after steam loss)	0-250 °C	(b)
<u>Na - K (low albite / K - feldspar)</u>			
$t\text{ }^{\circ}\text{C} = 933/(0.993 + \log \text{Na/K}) - 273.15$		25-250 °C	(a)
$t\text{ }^{\circ}\text{C} = 1319/(1.699 + \log \text{Na/K}) - 273.15$		250-350 °C	(a)
$t\text{ }^{\circ}\text{C} = 1217/(1.483 + \log \text{Na/K}) - 273.15$		>150 °C	(c)
$t\text{ }^{\circ}\text{C} = 855.6/(0.8573 + \log \text{Na/K}) - 273.15$		>150 °C	(d)
<u>Na - K - Ca</u>			
$t\text{ }^{\circ}\text{C} = 1647/(\log \text{Na/K} + \beta[\log(\sqrt{\text{Ca/Na}}) + 2.06] + 2.47) - 273.15$		<100°C $\beta = 4/3$	(e)
>100°C $\beta = 1/3$			

(a) Arnórsson et al. 1983, (b) Fournier (1977), (c) Fournier (1979), (d) Truesdell (1975), (e) Fournier and Truesdell (1973).

### 4.3 Mixing

Pressure decline during exploitation often leads to inflow of cold groundwater in the shallow part of the hydrothermal system which then mixes with the hot water. Mixing models may then be applied to evaluate the mixing ratios. A simple method of calculation uses a plot of dissolved silica vs. the temperature of the water (Fournier and Truesdell, 1974, Truesdell and Fournier, 1977). This is based on the solubility of the silica minerals quartz and chalcedony (Figure 5). A straight line is drawn from a point representing the non-thermal component of the mixed water through the mixed water to intersect with the solubility curve of the silica minerals.

## 5. CHANGES OF CHEMISTRY DUE TO EXPLOITATION

After production has been initiated, chemical analysis of geothermal water can give valuable information about the changes occurring during utilization. Long-term exploitation may cause a pressure drop or draw-down in the system. This causes the surface activity to change or disappear. In some instances the pressure draw-down creates a potential danger for inflow of colder groundwater or seawater into the system followed by cooling and sometimes changes of production characteristics.

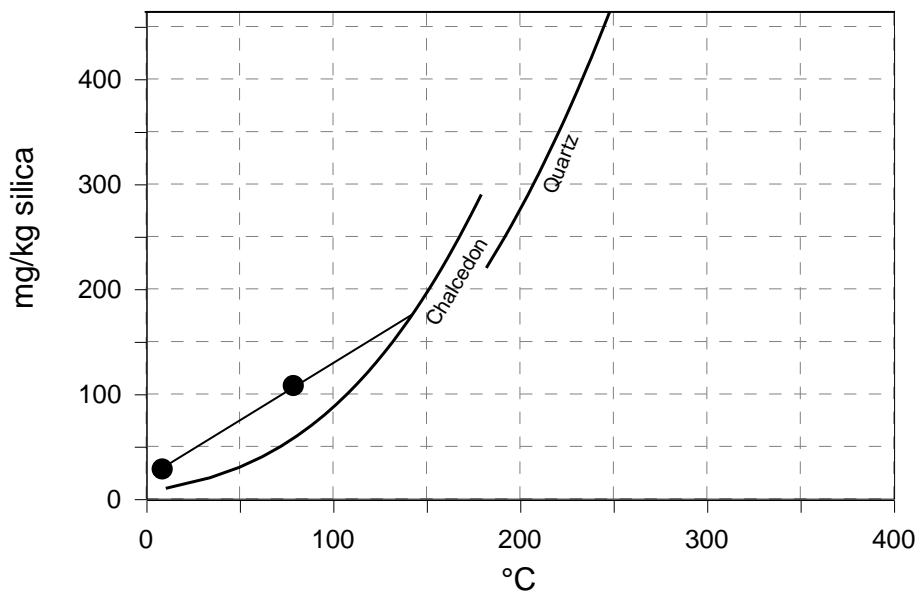


FIGURE 5: Silica mixing model

The concentration of most elements in geothermal water is dependent on temperature. Mixing of geothermal water and colder water often causes deviation from equilibrium. Changes in the chemical composition of geothermal water caused by invasion of cold ground water may precede physical changes. The results of chemical changes may be potential corrosion and scaling.

The main chemical components in geothermal water are silica ( $\text{SiO}_2$ ), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), carbonate (total  $\text{CO}_2$ ), hydrogen sulphide ( $\text{H}_2\text{S}$ ), sulphate ( $\text{SO}_4$ ), chloride (Cl) and fluoride (F). The changes in chemistry due to exploitation are primarily caused by invention and mixing of other water types. Most often this is cold water but sometimes it may have undertaken some changes towards mineral equilibrium. Knowledge of the cold freshwater composition is important for the evaluation of mixing during exploitation. The following elements have proved to be valuable in the chemical monitoring of exploited geothermal fields. The elements which are controlled by equilibrium with few minerals are usually first to show changes.

Chloride (Cl) is in many cases suitable for determining mixing if the chemistry of the thermal water has a different composition than the cooler water which it is mixed with. Cold groundwater often has lower chloride concentration than geothermal water. The infiltration of seawater into a freshwater geothermal system is often easily traced. The inflow of cold freshwater into a geothermal system is often difficult to detect at an early stage.

Silica ( $\text{SiO}_2$ ) is one of the main constituents in geothermal water. Its concentration is controlled by the silica minerals quartz and chalcedony and is commonly used as a geo-thermometer. The concentration of silica increases with increasing temperature. Therefore mixing with cooler fluid will in all cases reduce the concentration of silica. The silica mixing model (Figure 5) could be applied to estimate the ratios of geothermal water and the cooling fluid.

Magnesium (Mg) in geothermal water is controlled by the formation of alteration minerals such as clays. Its concentration is usually very low in geothermal water but higher in cold freshwater. Mixing of geothermal water and fresh water or saline water would increase the concentration of magnesium in the exploitable water.

Hydrogen sulphide ( $\text{H}_2\text{S}$ ) is often present in geothermal water but not in cold freshwater. A decrease in hydrogen sulphide in the geothermal water with time is therefore an indication of dilution. Mixing of



cold freshwater with geothermal water containing hydrogen sulphide may increase the sulphate concentration where cold water is commonly saturated with dissolved oxygen and it would react with hydrogen sulphide forming sulphate. But it should be kept in mind that an increase in sulphate is usually very low and is in most cases hardly seen in increasing sulphate.

*Fluoride (F)* may have a different composition in cold freshwater as opposed to geothermal water. In Iceland the concentration of fluoride in cold fresh water is very low (<0.1 mg/kg). Geothermal water contains on the other hand commonly 1-2 mg/kg and mixing with cold water would then reduce the fluoride content.

*Dissolved oxygen* decreases in water with increasing temperature. Most geothermal water is free of dissolved oxygen but mixing with cold freshwater could lead to the dissolved oxygen being detected. Increasing dissolved oxygen in the fluid would certainly decrease the content of hydrogen sulphide in the geothermal water. If the geothermal water is free of hydrogen sulphide and any dissolved oxygen is entering the water for example through mixing it will remain in the water and may cause corrosion.

## 6. CORROSION

Corrosion has been experienced in association with water containing dissolved oxygen at low temperatures (< 80°C), carbon dioxide (pH<8.5) waters below 100 °C and water with a rather high chloride content. Corrosion is one of the parameters that often follows mixing of fresh water and geothermal water where dissolved oxygen increases. A very slight increase in salinity will catalyze oxygen corrosion considerably. If dissolved oxygen is detected it will result in increased corrosion.

To avoid corrosion the dissolved oxygen has to be removed. This can be done by boiling or adding chemicals, which react with the oxygen. Addition of sodium sulphite to the water (10 ppm Na<sub>2</sub>SO<sub>3</sub> per 1 ppm O<sub>2</sub>) is widely used. The dissolved oxygen is then removed owing to the reaction:



Dissolved oxygen and hydrogen sulphide cannot exist together in solution (or only to a certain extent). Sulphide is therefore a good natural eliminator of dissolved oxygen if it enters the system from the atmosphere for example in storage tanks. The empirical results from Reykjavik Energy show that 1.6 ppm of hydrogen sulphide is needed to remove 1 ppm of dissolved oxygen. An example of using natural hydrogen sulphide to eliminate dissolved oxygen is shown in section 8.2.

Copper and copper alloys are widely used in district heating systems, e.g. in pipes, valves, flow meters, heat exchangers and pumps. It has long been recognized that copper corrodes in a sulphide containing environment. In sulphide containing environments the copper becomes coated, almost at once with a thin black coating of copper sulphide, which is easily removed with the flowing water resulting in further corrosion of the metal. Copper pipes should therefore be avoided if the water contains hydrogen sulphide.

## 7. SCALING

Troublesome scaling of calcite and silica minerals is often associated with the utilization of geothermal fluid. 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 depositing rate.

## 7.1 Calcite

Calcite is the most common scaling product. The solubility of calcite as a function of temperature is shown in Figure 6. 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:



The equilibrium constant for the reaction is

$$K_{\text{calcite}} = a_{\text{Ca}^{++}} \cdot a_{\text{CO}_3^{--}} \quad (5)$$

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

$$Q_{\text{calcite}} = a_{\text{Ca}^{++}} \cdot a_{\text{CO}_3^{--}} \quad (6)$$

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 has to be reached before deposition forms.

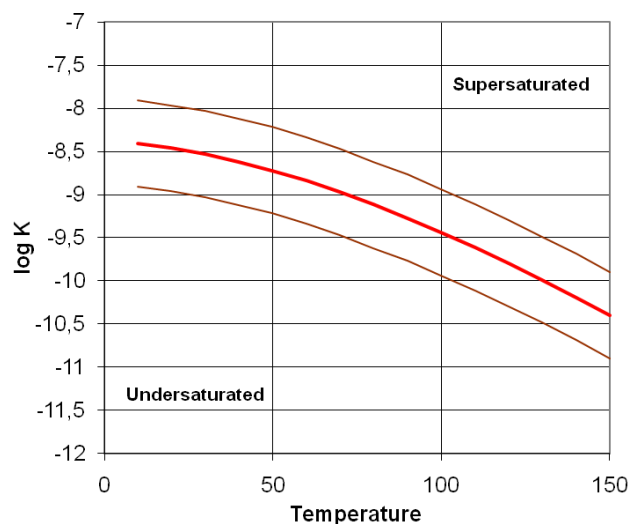


FIGURE 6: Solubility of calcite. The red line represents the solubility and the brown lines the division of error for the solubility.

Figure 7 shows the affect 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 deaerated 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 far the strongest at the first level of boiling. The magnitude of calcite supersaturation caused by boiling depends on the salinity of the unboiled water and its temperature. Strongest supersaturation is produced at the lowest temperatures and at the highest salinity. The mixing of inflow from two or more aquifers, each with 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.

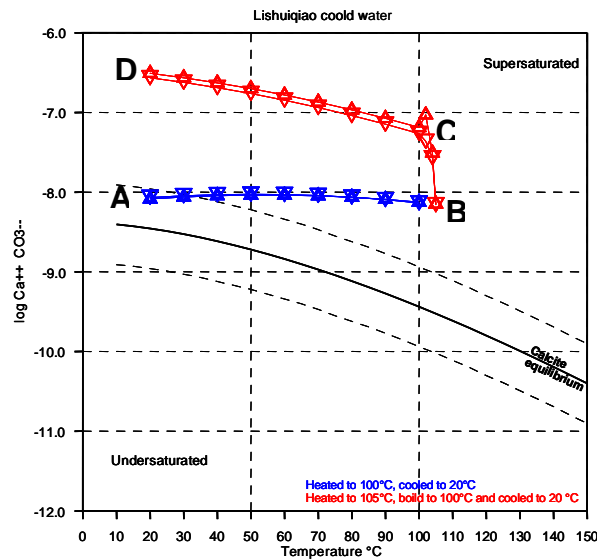


FIGURE 7: Solubility of calcite. Example of heating, boiling and cooling of groundwater

The pH of water highly affects the calculated solubility of calcite. Therefore it is important to have reliable determination of the pH. It changes during storage if special precaution is not taken. Therefore it is often measured in the field during the collection of the sample. If that is not possible a cooled sample has to be collected in airtight bottles and brought to the laboratory where it should be determined as soon as possible. Figure 8 shows an example where pH had been determined in laboratory without keeping the sample in airtight bottle and how the calcite solubility changed by just changing pH determined at the field. All other components were kept the same. For the first case the water calculated to be supersaturated and calcite scaling should be expected. On the other hand no calcite scaling was observed. When the pH was determined in the field and the calculations repeated with “new” pH-value the solubility calculated to be in equilibrium.

## 7.2 Silica

The concentration of silica increases with increasing temperature and it depends on the solubility of quartz and chalcedony (Figure 3). During cooling the silica is in solution until solubility of amorphous silica is reached. At still lower temperature the water is 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. Therefore silica depositions should not be expected in low temperature waters. 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 increases due to steam loss and the amorphous silica saturation curve is reached at higher temperature.

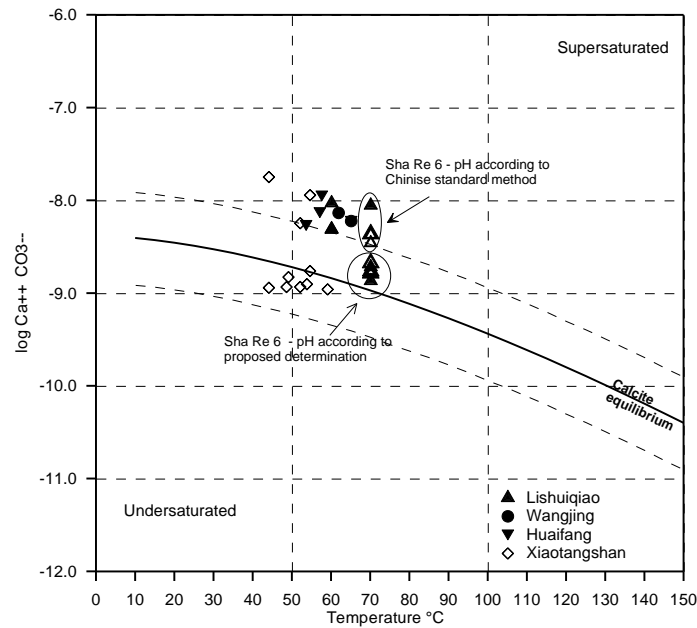
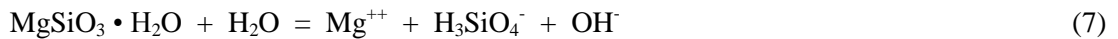


FIGURE 8: Solubility of calcite. Example of water with different pH

### 7.3 Magnesium silicate

Depositions of magnesium silicate can form where fresh groundwater is mixed with geothermal water. If the solubility of the product is known it is possible to perform similar calculation using the water analysis as described for calcite. The solubility of magnesium silicate can be described by the following reaction:



The equilibrium constant for reaction (6) is given by

$$K_{\text{Mg-silicate}} = a_{\text{Mg}^{++}} \cdot a_{\text{H}_3\text{SiO}_4^-} \cdot a_{\text{OH}^-} \quad (8)$$

Figure 9 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 as temperature.

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

$$Q_{\text{Mg-silicate}} = a_{\text{Mg}^{++}} \cdot a_{\text{H}_3\text{SiO}_4^-} \cdot a_{\text{OH}^-} \quad (9)$$

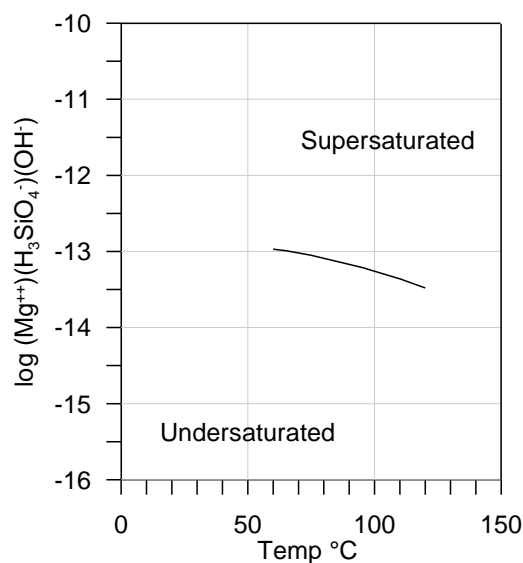


FIGURE 9: Solubility of magnesium silicate as a function of temperature

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

## 8. EXAMPLES OF CHEMICAL MONITORING

### 8.1 Cold water invasion

The district heating in Reykjavik, Iceland is utilizing three low temperature geothermal fields and one high-temperature geothermal field. All the low temperature fields were to some extent over exploited in the years 1985 to 1990. The pressure history of the Ellidaar field shows a rapid draw down and recovery each time the pumping from the field is changed. At a constant pumping rate for couple of months, pressure stabilization occurs, indicating a massive recharge of fluid to the reservoir. Monitoring of production, temperature and chemistry shows that the recharge is of groundwater origin. Figure 10 shows the changes in temperature, silica, chloride and fluoride content with time for one of the drill hole in the area. Cooling of up to 20 °C has been observed since 1968. The concentration of silica and fluoride has decreased at the same time. Only slight changes have on the other hand been in the concentration of chloride where the chloride concentration in the groundwater and in the geothermal water is similar.

Due to the recharge the concentration of dissolved oxygen has increased drastically making the water corrosive to steel. The corrosion has been avoided by mixing the geothermal water from the Ellidaár field with water from other geothermal fields containing hydrogen sulphide ( $H_2S$ ). Hydrogen sulphide reacts fast with dissolved oxygen until either of the components is dissipated.

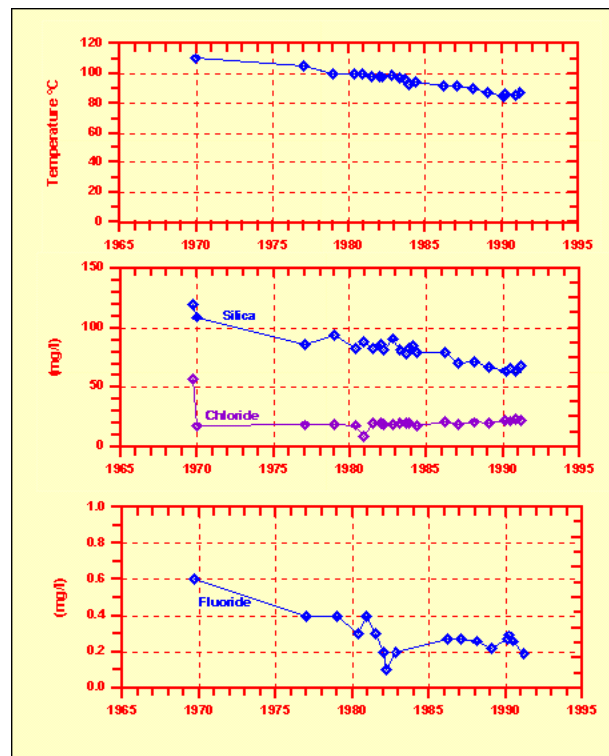


FIGURE 10: Changes in temperature, silica, chloride and fluoride in well 30 at Elliðaár field

## 8.2 Elimination of dissolved oxygen by natural hydrogen sulphide

Chemical monitoring during geothermal utilization covers more than just monitoring of the geothermal field and how the utilization changes reservoir parameters. Regular monitoring of production related parameters has to be carried out. These parameters determine the quality of the water and steam used in different applications. Examples of these are dissolved oxygen, hydrogen sulphide ( $H_2S$ ) and pH in low temperature water in direct use applications and gas composition and carry-over of high temperature steam.

As mentioned in an earlier section dissolved oxygen and hydrogen sulphide cannot exist together in a solution. Reykjavík Energy is using three low temperature areas for district heating. The geothermal water at Reykir and Reykjahlíð in Mosfellsveit contain hydrogen sulphide and is free of dissolved oxygen. This water is piped to storage tanks (Figure 11) where atmospheric oxygen can enter. The hydrogen sulphide reacts with the oxygen which dissolves in the water. During this process the concentration of hydrogen sulphide decreases and the water will still be free of dissolved oxygen. The pipeline from the Reykir – Reykjahlíð field passes through another geothermal field, Elliðaárfield. The water there contains some dissolved oxygen but no hydrogen sulphide. The water from these two fields is then mixed together. After mixing all the dissolved oxygen has been eliminated and the concentration of hydrogen sulphide has decreased. After this the water is then stored in storage tanks where atmospheric oxygen can enter. After the last storage tanks the water still contains some hydrogen sulphide and is free of dissolved oxygen.

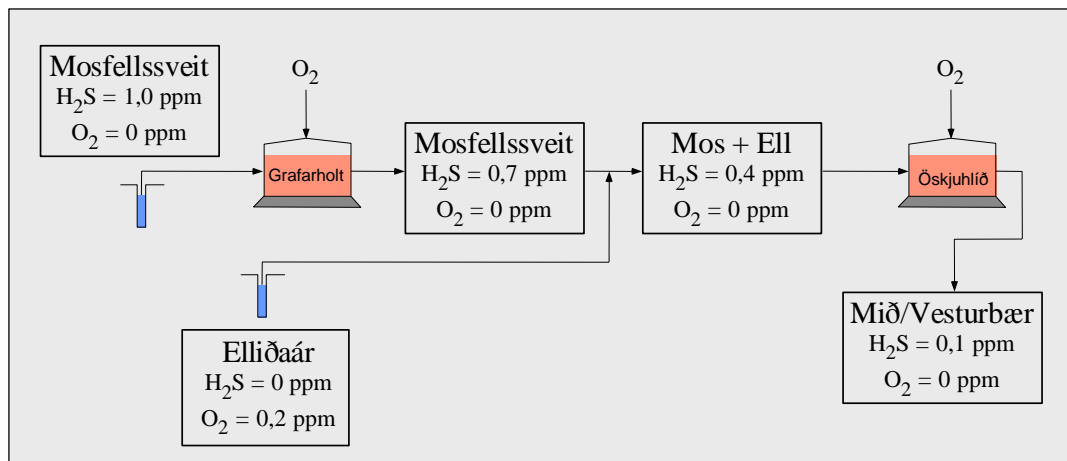


FIGURE 11: Elimination of dissolved oxygen using H<sub>2</sub>S in geothermal water

## 9. CONCLUSION

Chemistry of geothermal fluid is an important factor during exploration and development of geothermal resources. It can be used in exploration to predict underground temperature and distinguish the origin of the water. During development it can be used to predict scaling of different components by comparing the water chemistry to theoretical solubility of minerals. During the exploration phase the chemistry is the key factor to solve problems during utilization. All the interpretation is based on the quality of the analyses. The analyses of the elements are usually of high quality in the laboratory. But the analyses are only representative of the sample reaching the laboratory. More often the sample changes after collection during storage. It is therefore essential to plan carefully the collection of samples and treat the sample in the field to avoid these changes. This is especially important for volatile components which then may change the pH of the water. All chemical reactions are more or less dependant of the pH. Therefore interpretation of mineral equilibria and prediction of scaling will give confusing results if samples have degassed during storage.

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