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CHEMICAL ASPECTS AND METHODS IN GEOTHERMAL EXPLORATION AND USE

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ABSTRACT

Geochemistry plays an important role in geothermal exploration, drilling and management of geothermal reservoirs. In this summary some methods of the use of chemical analysis will be mentioned, such as geothermometers, mineral equilibria, scaling and corrosion. Special emphasis is on the quality of data and how that affects the interpretation.

INTRODUCTION

The use of geochemistry starts in early surface exploration, continues through all phases of preparation for utilization and plays an important

role during all the utilization through monitoring and reservoir management. The process of exploring, developing and utilization of geothermal resources can be divided into four main phases, (a) surface exploration, (b) exploratory drilling, (c) production drilling and (d) utilization. The boundaries between the phases are not always clear. The results of the exploratory drilling may raise questions which may demand further surface exploration. The exploratory drilling phase ends when enough data has been obtained to locate potential production site. If exploratory drilling is very successful it may lead to direct utilization on small scale.

Table 1. Main tasks of water chemistry in geothermal exploration, drilling, development and utilization

Surface exploration	Exploratory drilling
Evaluate origin of water	Assess reservoir water composition with reference to utilization
Estimate underground temperature	Establish understanding of water composition through mineral/water equilibria
Cold water composition	Estimate water temperature at the point of well inflow
Map the extent of the geothermal system	Evaluate if boiling in the reservoir affects the water chemistry
Characterize the reservoir chemistry with respect to utilization	Define scaling and corrosion problems
Define environmental impact of the utilization	Revise environmental impact of the utilization
Production drilling	Utilization
Establish changes in total well discharge composition during long term testing	Monitor chemical composition of well discharges
Participate in scaling and corrosion tests	Monitor chemical parameters of fluid in the distribution system
Participate in working out methods for disposal of waste fluid	Participate in solving problems arising from utilization
Provide chemical data on fluid composition relevant for construction design	

This is often the case with low enthalpy geothermal resources. The water chemistry is relevant for all the phases and the geochemist participates in all the phases involved in research and utilization. Table 1 summarizes the task of water chemistry in these four phases of development of geothermal resources.

The geochemist together with other geothermal specialists delineate model of the geothermal system, which have 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 production of the reservoir. It is also important for further construction design and to evaluate scaling and corrosion.

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.

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 pressure drop or drawdown in the system. This causes the surface activity to change or disappear. In some instances the pressure drawdown creates a potential danger for inflow of colder groundwater or seawater into the system followed by cooling and sometimes change of production characteristics.

Geochemical studies of geothermal fluids essentially involve three main steps. These are:

- Collection of samples
- Chemical analyses

- Interpretation of the data
- Collection of samples requires 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 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 are 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.

COLLECTION OF WATER FROM LOW-TEMPERATURE GEOTHERMAL RESOURCES

Here only the collection of low-temperature geothermal water will be discussed. 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.

Once learned, the collection of water is a routine procedure and should be described similarly as analytical methods in 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 components samples for isotopic determination may be collected as well as for various trace elements.

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

Table 2. Main chemical components analysed in low-temperature geothermal water

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 (O₂) and hydrogen sulphide (H₂S). Sometimes pH and total carbonate is also determined on-site.

During collection the sample have to be cooled, especially for the volatile components. If pH, total carbonate and hydrogen sulphide is going to be analysed in laboratory, the sample have to be cooled and stored in air-tide 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

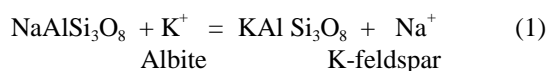
spite of accurate analyses of the water in the bottle the result is not representing the spring or the well. During storage the volatiles degasses and the recorded values cannot be used in detailed evaluation of the sample. It should be kept in mind that accurate determination of the pH is essential for all further calculations since it participates in almost all chemical reactions.

The sample collected for determination of cation has to be filtrated and acidified to avoid precipitation. Usually samples for determination of sulphate can be collected without any treatment. But if the concentration of hydrogen sulphide (H_2S) is high it can oxidize and then increase the concentration of sulphate. In that case hydrogen sulphide (H_2S) have to be precipitated for example by adding zink-acetate, $Zn(CH_3COO)_2$. If the temperature is high and the silica (SiO_2) concentration is expected to exceed 100 mg/l silica may polymerise and even precipitate during storage. In such a case the sample for determination of silica have to be diluted if spectrophotometric methods are going to be used.

MINERAL EQUILIBRIA

The composition of geothermal fluid is controlled by 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 temperature above 280°C the type of rock is insignificant but at lower temperature it is most pronounced.

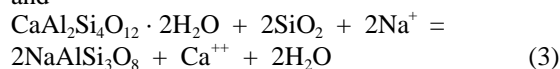
Chemical equations for formation of alteration minerals can be written to which the water composition is compared. For example at equilibrium, ratios of sodium and potassium in solution are controlled by temperature dependent exchange reaction:



and the equilibrium constant for the reaction is written as:

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

and



and the equilibrium constant for the reaction is written as:

$$K_{eq} = [Ca^{++}][H_2O]^2 / [Na^+]^2 \quad (4)$$

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 (Helgeson 1969, Helgeson et al. 1969, Robie et al. 1978).

The activity ratios of aqueous species can also be compared to theoretical activity phase diagrams (Bowers et al. 1984). Fig. 1 shows a phase diagram at 260°C and saturated water vapour pressure for system Na_2O - K_2O - Al_2O_3 - SiO_2 - H_2O . The diagram is derived from experimental phase equilibrium data for the coexistence of K-mica, K-feldspar, and albite (Brown and Ellis, 1970).

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). For Icelandic waters the equilibrium has been presented by temperature dependent graphs of cation/proton ratios (Fig. 2) and concentration of dissociated weak acids (Fig. 3) from geothermal well discharges (Arnórsson et al., 1983). The equations describing the temperature dependence of the cation/proton ratios and undissociated weak acid concentrations are listed in table 3. These graphs are examples showing what can be used to study equilibrium but many others graphs can be used.

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

The concentration and 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.

CHEMICAL GEOTHERMOMETERS

Chemical geothermometers are in one way or the other based on chemical equilibrium. The equations used are either obtained directly from thermodynamic data of known chemical reactions or as empirical relations. The most widely used chemical geothermometers are the silica geothermometers, the Na-K and the Na-K-Ca geothermometers. Table 4 summarizes some of the equations commonly used as chemical geothermometers for geothermal water.

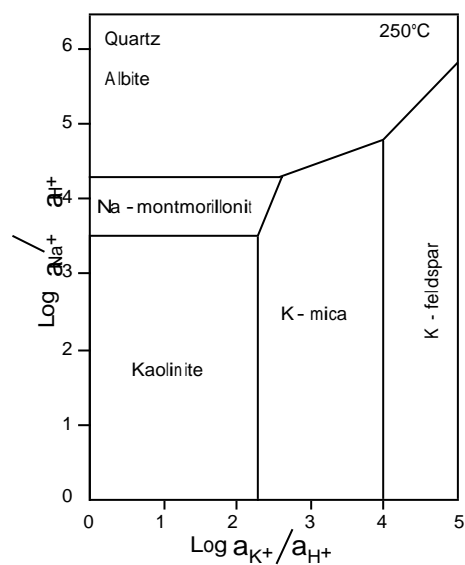


Figure 1. Activity diagram for principal phases in the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 250°C .

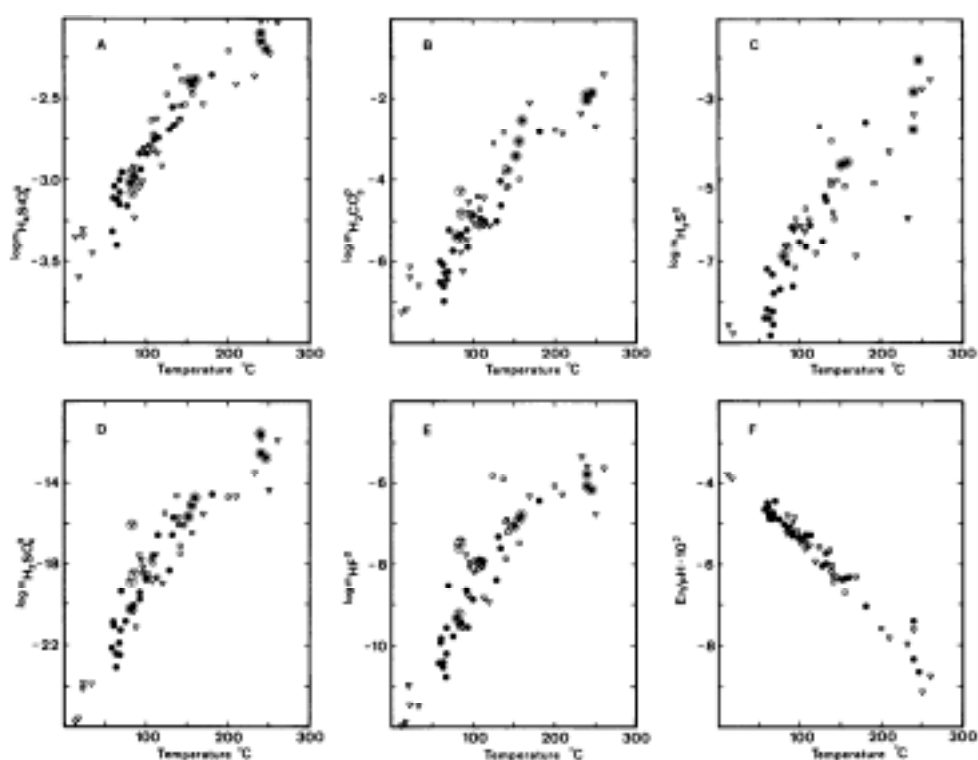


Figure 3. Variation with temperature of undissociated acid concentration in geothermal waters. Filled circles represent unmixed drill hole discharges with well defined temperature (Arnórsson et al. 1983)

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
$\log \text{H}_4\text{SiO}_4^0$	$-0.588 - 0.00441T - 1515.21/T + 1.3470 \log T$
$\log \text{H}_2\text{CO}_3^0$	$-1.794 - 0.00510T - 4469.63/T + 4.1414 \log T$
$\log \text{H}_2\text{S}^0$	$-1.678 - 0.00355T - 5071.05/T + 3.8889 \log T$
$\log \text{H}_2\text{SO}_4^0$	$-6.436 - 0.03906T - 13335.68/T + 14.7958 \log T$
$\log \text{HF}^0$	$-5.262 - 0.03511T - 7964.11/T + 12.1022 \log T$
$\log \text{Na}^+/\text{H}^+$	$2.694 + 0.0223T + 4243.47/T - 6.2069 \log T$
$\log \text{K}^+/\text{H}^+$	$2.505 + 0.01971T + 3325.71/T - 5.7814 \log T$
$\log \sqrt{\text{Ca}^{+2}/\text{H}^+}$	$1.733 + 0.01117T + 3890.15/T - 3.9977 \log T$
$\log \sqrt{\text{Mg}^{+2}/\text{H}^+}$	$1.816 + 0.01078T + 3727.48/T - 4.1640 \log T$
$\log \sqrt{\text{Fe}^{+2}/\text{H}^+}$	$-4.696 - 0.04273T - 1011.46/T + 10.8032 \log T$
$\log \text{Al}(\text{OH})_4^-/\text{OH}^-$	$-3.407 - 0.02364T - 3417.36/T + 7.8426 \log T$

The silica geothermometers is based on experimentally determined solubility of the silica minerals chalcedony and quartz and the dissolved silica in the geothermal water is correlated with the solubility of these minerals. 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 geothermometers 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 4 shows the solubility curves of quartz, chalcedony as a function of temperature. Dilutions of the geothermal water with cold or slightly heated un-equilibrated groundwater affect the silica-geothermometer. If chemical equilibrium is attained after mixing the silica geothermometer will give the temperature of the last equilibrium after mixing. If equilibrium is not attained lower values will be obtained by the silica geothermometer. To deal with such water mixing models have been applied.

The Na-K geothermometer is based on temperature dependence of partitioning of sodium and potassium between the fluid and alkali feldspars. Figure 5 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.

When different chemical geothermometers give different estimates the information can be used to formulate a model of the geothermal system, where different geothermometers may indicate mixing and different temperature in different parts of the reservoir.

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. 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 (fig. 6). A straight line is drawn from a point representing non-thermal component of the mixed water through the mixed water to intersect with the solubility curve of the silica minerals.

The chemistry of thermal water is determined by the rate of leaching of the various chemical components for the primary rock constituents, fluid flow into the system and formation of alteration minerals. Equilibrium is attained or closely approached with respect to all major components, at least in the temperature interval of 50 – 250 °C. The variables controlling the chemistry are temperature, pressure and the availability of the mobile component, chloride.

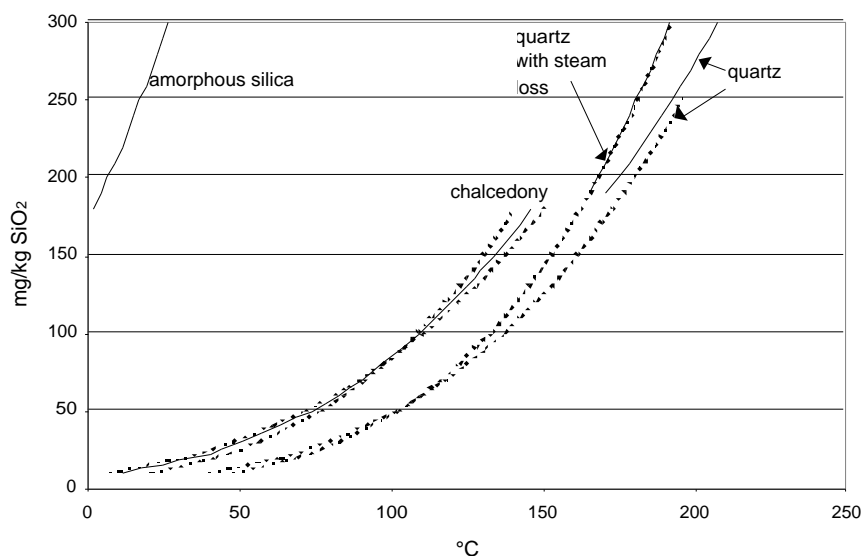


Figure 4. Solubility of quartz, chalcedony and amorphous silica as a function of temperature. The silica concentration is that of un-dissociated silica.

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

CHALCEDONY

$t\text{ }^{\circ}\text{C} = 1112/(4.91 - \log \text{SiO}_2) - 273.15$	25-180 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1264/(5.31 - \log \text{SiO}_2) - 273.15$	(after steam loss) 100-180 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1032/(4.69 - \log \text{SiO}_2) - 273.15$	25-180 $^{\circ}\text{C}$	(b)

QUARTZ

$t\text{ }^{\circ}\text{C} = 1164/(4.90 - \log \text{SiO}_2) - 273.15$	180-300 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1498/(5.70 - \log \text{SiO}_2) - 273.15$	(after steam loss) 180-300 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1309/(5.19 - \log \text{SiO}_2) - 273.15$	0-250 $^{\circ}\text{C}$	(b)
$t\text{ }^{\circ}\text{C} = 1522/(5.75 - \log \text{SiO}_2) - 273.15$	(after steam loss) 0-250 $^{\circ}\text{C}$	(b)

AMORPHOUS SILICA

$t\text{ }^{\circ}\text{C} = 731/(4.92 - \log \text{SiO}_2) - 273.15$	25-180 $^{\circ}\text{C}$	(b)
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NA – K (LOW ALBITE / K - FELDSPAR)

$t\text{ }^{\circ}\text{C} = 933/(0.993 + \log \text{Na/K}) - 273.15$	25-250 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1319/(1.699 + \log \text{Na/K}) - 273.15$	250-350 $^{\circ}\text{C}$	(a)
$t\text{ }^{\circ}\text{C} = 1217/(1.483 + \log \text{Na/K}) - 273.15$	>150 $^{\circ}\text{C}$	(c)
$t\text{ }^{\circ}\text{C} = 855.6/(0.8573 + \log \text{Na/K}) - 273.15$	>150 $^{\circ}\text{C}$	(d)

NA – K – CA

$t\text{ }^{\circ}\text{C} = 1647/(\log \text{Na/K} + \beta[\log(\sqrt{\text{Ca/N}}) + 2.06] + 2.47) - 273.15$	<100 $^{\circ}\text{C}$ $\beta = 4/3$	(e)
>100 $^{\circ}\text{C}$ $\beta = 1/3$		

(a) Arnórsson et al. 1983, (b) Fournier (1977), (c) Fournier (1979), (d) Truesdell (19??), (e) Fournier and Truesdell (1973).

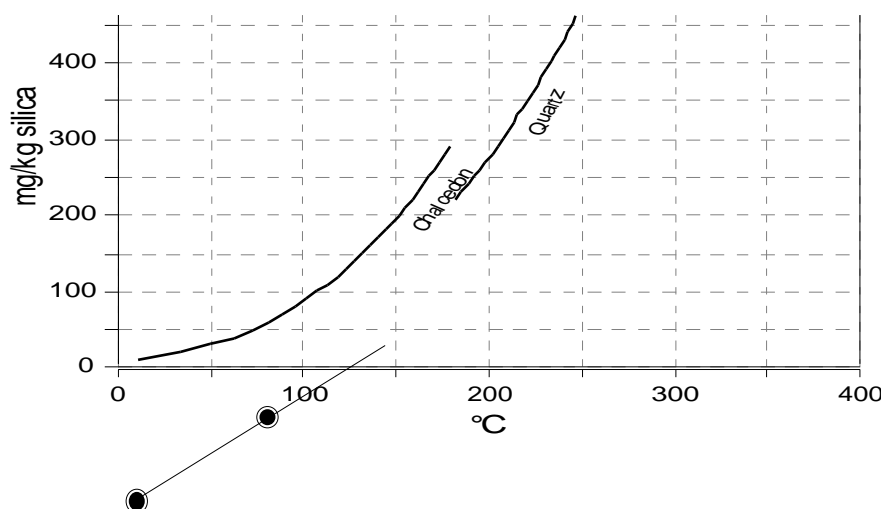


Figure 6. Silica mixing model

Changes in chemistry due to exploitation

The main chemical components in geothermal water are silica (SiO_2), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), carbonate (total CO_2), hydrogen sulphide (H_2S), sulphate (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 sometime 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 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 determine mixing if the chemistry of the thermal water has 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 (SiO_2) is one of the main constituents in geothermal water. Its concentration is controlled by the silica minerals quartz and chalcedony. 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 could be applied to estimate

the ratios of geothermal water and the cooling fluid.

Magnesium (Mg) in geothermal water is controlled by 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 (H_2S) is often present in geothermal water but not in cold freshwater. Decreasing in hydrogen sulphide in the geothermal water with time is therefore 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 increase in sulphate is usually very low and is in most cases hardly seen in increasing sulphate.

Fluoride (F) may have different composition in cold freshwater and 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 (fig 7). Most geothermal water is free of dissolved oxygen and mixing with cold freshwater could lead to that dissolved oxygen

would be detected. Increasing dissolved oxygen in the fluid would certainly decrease the content of hydrogen sulphide in the geothermal water. Some geothermal water are free of hydrogen sulphide and any dissolved oxygen entering the water will remain in the water.

CORROSION

Corrosion has been experienced in association

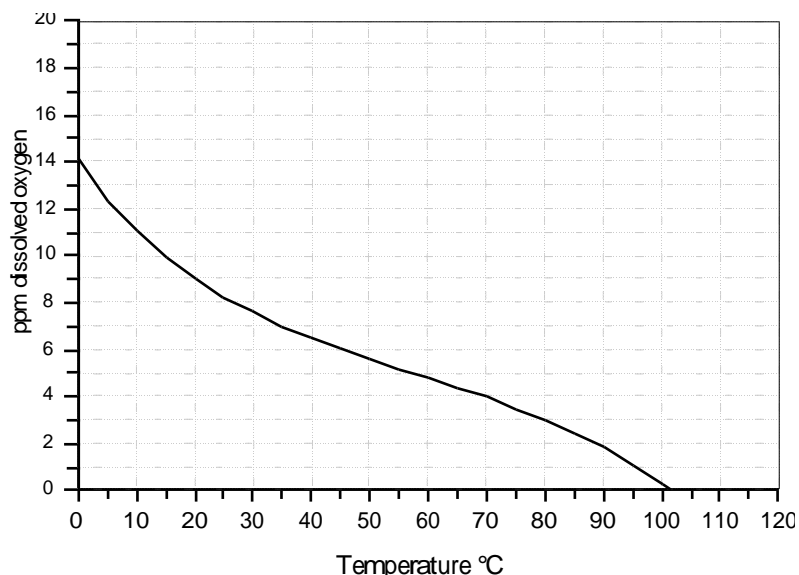


Figure 7. Solubility of dissolved oxygen in water at 1 bar pressure.

SCALING

Troublesome scaling of calcite and silica minerals are 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 deposition rate.

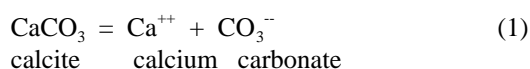
Calcite

Calcite is the most common scaling product. The solubility of calcite as function of temperature is shown in fig. 8. 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.

with water containing dissolved oxygen at low temperatures (< 80°C), carbon dioxide waters below 100 °C and water with rather high chloride.

Corrosion is one of the parameters often follows mixing of fresh water and geothermal water where dissolved oxygen is increased. A very slight increase in salinity will catalyze oxygen corrosion considerably. If dissolved oxygen is detected it will result in increased corrosion.

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



The equilibrium constant for the reaction is

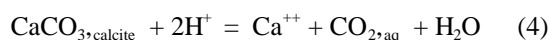
$$K_{\text{calcite}} = a_{\text{Ca}^{++}} \cdot a_{\text{CO}_3^{--}} \quad (2)$$

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

$$Q_{\text{calcite}} = a_{\text{Ca}^{++}} \cdot a_{\text{CO}_3^{--}} \quad (3)$$

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.

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



The equilibrium constant for reaction (4) is given by

$$K_{\text{calcite}} = a_{\text{Ca}^{++}} / a_{\text{H}^+}^2 \cdot a_{\text{CO}_{2, \text{aq}}} \quad (5)$$

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

$$K_{\text{H}_2\text{CO}_3} = a_{\text{H}^+} \cdot a_{\text{HCO}_3^-} / a_{\text{H}_2\text{CO}_3} \quad (6)$$

The second dissociation constant is then

$$K_{\text{HCO}_3^-} = a_{\text{H}^+} \cdot a_{\text{CO}_3^{--}} / a_{\text{HCO}_3^-} \quad (7)$$

From these equations 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 lead to supersaturation of that mineral.

Figure 8 shows also 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 under-saturated, becomes slightly super-saturated. 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 highest salinity.

For calculation of this type some of the computer programs previously mentioned can be used. The WATCH programme (Arnórsson et al., 1982) has been used for the calculations shown here. 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. Dissolution of calcium from asbestos pipelines can increase the solubility product of calcite which may cause supersaturation and formation of calcite depositions.

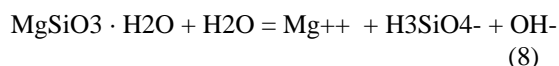
Silica

The concentration of silica increases with increasing temperature and it depends on the solubility of quartz and chalcedony (fig. 4). During cooling the silica is in solution until solubility of amorphous silica is reached. At still lower temperature the water is super-saturated 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 increases due to steam loss and the amorphous silica saturation curve is reached at higher temperature.

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:



The equilibrium constant for reaction (8) is given by:

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

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 temperature.

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

$$Q_{\text{Mg-silicate}} = a_{\text{Mg}^{++}} \cdot a_{\text{H}_3\text{SiO}_4^-} \cdot a_{\text{OH}^-} \quad (10)$$

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

Cold fresh groundwater always contains some magnesium but the concentration of silica is relatively low. If cold water is heated and deaerated through boiling the pH of the water increases. 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 under-saturated 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.

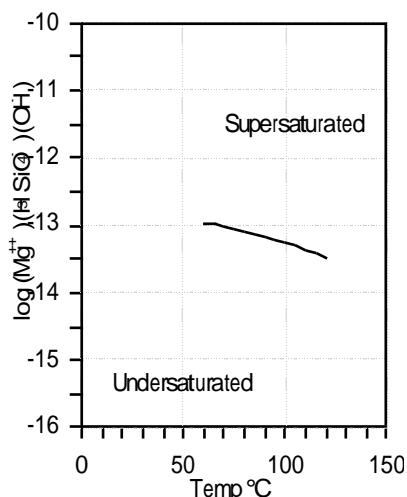


Figure 9. Solubility of magnesium silicate as a function of temperature.

References

- Arnórson, S., Sigurðsson, S. and Svavarsson, H., 1982. The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°C. *Geochim. Cosmochim. Acta*, **46**, 1513-1532.
- 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.
- Arnórsson, S., Gunnlaugsson, E. and Svavarsson, H., 1983. The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta*, **47**, 567-577.
- Arnórsson, S. and Gunnlaugsson, E. 1985. New gas geothermometers for geothermal exploration – Calibration and application. *Geochim. Cosmochim. Acta*, **49**, 1307-1325.
- Bowers, T. S., Jackson, K. J. and Helgeson, H. C., 1984. *Equilibrium Activity Diagrams for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 60°C*. Springer-Verlag, Berlin, 397 pp.
- Brown, P. R. L. and Ellis, A. J., 1970. The Ohaki-Broadlands hydrothermal area, New Zealand, mineralogy and related geochemistry. *Am. J. Sci.*, **269**, 97-131.
- Brown, P. R. L., 1978. Hydrothermal alteration in active geothermal fields. *Annual Review in Earth and Planetary Sciences*, **6**, 229-250.
- Fournier, R.O., 1977. Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, **5**, 41-50.
- Fournier, R.O., 1979. A revised equation for the Na/K geothermometer. *Geothermal Resources Council Transactions*, **3**, 221-224.
- Fournier, R. O. and Truesdell, A. H., 1973. An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, **37**, 1255-1275.
- Fournier, R. O. and Truesdell, A. H., 1974. Geochemical indicators of subsurface temperature – Part 2, estimation of temperature and fraction of hot water mixed with cold water. *J. Res. U.S. Geological Survey*, **2**, 263-270.
- 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.
- Kharaka, Y. K. and Barnes, I., 1973. SOLMNEQ: solution-mineral equilibrium computation. *National Tech. Infor. Serv. Tech. Rept.*, PB214-899, 82 pp.
- Michard, G., 1991. The physical chemistry of geothermal systems. In: F. D'Amore (coordinator) *Application of Geochemistry in Geothermal Reservoir Development*. UNITAR-UNDP Publication, Rome, 197-214.
- Plummer, L. N., Jones, B. F. and Truesdell, A., H., 1976. WATEQF – a fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *U.S. Geol. Surv. Water Resour. Invest.*, **76-13**, 61pp.
- 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.
- Truesdell, A. H. and Fournier, R. O., 1977. Procedure for estimating the temperature of a hot water component in mixed water using a plot of dissolved silica vs. enthalpy. *J. Res. U.S. Geological Survey*, **5**, 49-52.
- Truesdell, A. H. and Jones, B. F., 1974. WATEQ, a computer program for calculating chemical equilibria of natural waters. *J. Res. U.S. Geol. Surv.*, **2**, 233-248.