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# INJECTION OF WASTE GEOTHERMAL FLUIDS: CHEMICAL ASPECTS

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**Key words:** Scaling, injection, mineral saturation, amorphous silica, calcite, Krafla

**ABSTRACT**. Deposition of solids from geothermal waters, which occurs when they boil and change temperature, often leads to the formation of troublesome scales. The scale forming solids include “simple salts”, such as calcite, various sulphides and amorphous compounds (silica, Mg-silicate, Al-silicate). Data from Krafla, Iceland, Amatitlan, Guatemala and Momotombo, Nicaragua, have been used to demonstrate the value of chemical thermodynamic methodology to quantitatively assess scaling tendencies from geothermal waters. Such an assessment should be routinely carried out as a part of any geothermal development program to identify optimum conditions for injection of waste geothermal fluids and, at the same time, minimize the need for using inhibitors. The rate of scale formation depends on temperature, the aqueous concentrations of the scale forming components, the degree of supersaturation and kinetics. Desposition of amorphous silica from supersaturated water, which is probably the most troublesome scale, could possibly be reduced, even inhibited, by rapid cooling of the water to <50°C. Mixing of condensate and brine should always be considered as a possible means of preventing scaling in injection wells.

## 1. INTRODUCTION

Today it is the common practice to dispose of waste fluids from geothermal power plants by injection into special wells, both brine from producing wells and condensate from cooling towers and ejectors. Injection serves largely two purposes. It is environmentally desirable and helps maintaining reservoir pressures, at least, if the waste fluid is injected back into the reservoir, thus increasing its longevity, as well as the lifetime of individual production wells. In some producing geothermal reservoirs, however, natural recharge may be sufficiently high to make injection unimportant from the point of view of maintaining reservoir pressure.

There are essentially two problems associated with injection of waste geothermal fluids. One is scaling and the other thermal breakthrough. If the injected fluid flows rapidly into the aquifer of producing wells, it may not have had time to be heated sufficiently through contact with the reservoir rock, causing the performance of the affected production well to deteriorate, or even destroy it. For this reason injection is sometimes preferred on the boundaries of production wellfields or outside them, rather than within them.

The most troublesome scale which forms in surface equipment or in injection wells is amorphous silica. To avoid silica scaling from geothermal water, the common practice is to prevent it from cooling sufficiently to make it supersaturated with respect amorphous silica. This means that the waste water may be disposed of by injec-tion at temperatures as high as 180°C. Disposal of such a hot water entails poor use of heat from the geothermal fluid brought to the surface through drillholes. Improved heat extraction from high-temperature geothermal fluids and successful injection of cooled waste water requires improved theory and technology to cope with amorphous silica scale formation.

This contribution deals with scaling associated with injection of waste fluids from geothermal power plants, how to evaluate scaling tendencies from data on water and steam compositions followed by assessment of the best injection conditions.

## 2. SCALE FORMATION

The types of scales, which have been observed to form from geothermal waters within production wells, in surface equipment and in injection wells, include amorphous silica, calcite, anhydrite, various sulphides as well as silicates of magnesium and aluminium that are amorphous or largely amorphous, at least to X-rays (Arnórsson, 1981; Kristmannsdóttir, 1989). Equations describing the solubility of some of these minerals as a function of temperature are given in Table 1. It is not certain whether the amorphous Al-silicate scales represent a mechanical mixture of amorphous silica and Al-hydroxide, or if they are truly an aluminium silicate with a specific stoichiometry. Further studies, including experimental work, are needed to elucidate this. Data are not available on the solubility of a potential amorphous Al-silicate. In the present contribution formation of scales containing aluminium are assumed to involve precipitation of amorphous Al-hydroxide.

As geothermal waters boil and cool when they ascend from the reservoir to the surface, they become supersaturated with many hydrothermal minerals that are found in the reservoir rock, including quartz, Na- and K-feldspars, chlorite and epidote to mention some. However, these minerals have not been observed in scales. Evidently their precipitation is too sluggish to occur within the relatively short residence time of the geothermal water in production wells, surface equipment and injection wells.

Troublesome scales consist of amorphous phases, sulphides and “simple salts” (calcite, anhydrite) that evidently precipitate readily from supersaturated solution. The solubility of all these phases is temperature dependent and for some of them pH dependent as well. As a result their precipitation is brought about by boiling and/or temperature changes. The quantity of any particular scale that forms depends on the kinetics of precipitation and the concentration in the water of the scale forming components. Sulphide forming metals, such as iron and many base metals, occur in low concentrations in most geothermal waters. As a result the amount of sulphide scale that forms is limited. Metal mobility in saline geothermal waters is higher than in dilute ones. For this reason the quantity of sulphide deposits from saline waters is greater than from dilute ones. An extreme example is provided by the Salton Sea brine in southern California. Amorphous silica deposition provides an example of scaling that is controlled by kinetics rather than availability of the precipitating component.

Figure 1 depicts how the saturation state of common types of geothermal scale forming minerals changes during adiabatic boiling of aquifer water for 5 wells at Krafla, Iceland. Also shown is the saturation index for low-albite as an example of a hydrothermal mineral. The pattern seen for the various scale forming minerals is typical for geothermal waters in general. During the early stages of boiling the waters, which are initially close to being calcite saturated, become supersatured due to degassing. As boiling proceeds and the water cools, it changes towards a lower degree of supersaturation, even undersaturation due to the retrograde solubility of calcite. Cooling leads to decreasing amorphous silica undersaturation and even supersaturation, due to the prograde solubility of this phase. The situation for low-albite is the same but the reverse for anhydrite. In the case of amorphous Mg-silicate, whose solubility is pH-dependent, the pattern resembles that for calcite, except that the Mg-silicate solubility is prograde and for that reason the degree of undersaturation decreases progressively as the water cools by boiling. The solubility of amorphous Al-hydroxide is also prograde explaining a decreasing degree of undersat-uration towards lower temperature. During early stages of boiling, on the other hand, the Krafla well waters become more undersaturated with respect to Al-hydroxide as increase in pH (increase in $OH^-$) increases the solubility of this phase.

Changes in temperature alone change mineral saturation due to both solution pH and mineral solubility changes. An example is shown in Fig. 2 for water from the low pressure (120°C) separators of the Krafla power plant, Iceland. The water could be cooled by passing it through heat exchangers before injection with the purpose of exploiting its heat. Heating, on the other hand, would be expected to occur, if the water were injected from the separators into deep wells (hot rock).

## 3. LAYOUT OF INJECTION SCHEMES

Plans to inject waste geothermal water should include a chemical thermodynamic assessment of scaling tend-ncies. This involves calculation of mineral saturation indices for known scale forming minerals as a function of temperature and boiling. The WATCH aqueous speciation program (Arnórsson et al., 1982), version 2.1A (Bjarnason, 1994) has been used in the present study for this purpose. Other programs could have been used also, e.g. SOLVEQ (Reed and Spycher, 1984).

In some producing geothermal fields fluid from producing wells is conveyed to steam separators at each wellhead but in others the two phase fluid is piped from each well to separator stations where water from several wells mixes. The latter type of design is more attractive for injection as the water from many wells is gathered in one place where from it can be piped to injection wells.

Chemical thermodynamic assessment of mineral satura-tion should include every producing well in a specific wellfield because differences in fluid compositions and aquifer temperature between wells can cause much differ-ences in scaling tendencies upon boiling and changes in temperature of the water. To obtain the most reliable pre-diction of scaling tendencies it is best to collect water and steam samples at the same pressure. If fluid from many producing wells is conveyed to a steam separator station, samples of water and steam should also be collected of the mixed fluid to assess scaling tendencies of the mixed water

The assessment of mineral saturation should involve all potential scale forming phases and consider, (a) adiabatic boiling of the aquifer fluid (total discharge), (b) adiabatic boiling of separated water at a preselected pressure(s) and (c) temperature changes of the separated water. Results for calcite for well 1 at Amatitlan, Guatemala, shown in Fig. 3, have been used to demonstrate this.

If cold injection is desired, or mixing of brine with condensate considered feasible to avoid scaling, power generation using binary cycle should be taken into account or another use of the heat of the waste water.

## 4. THE EFFECTS OF MIXING CONDENSATE WITH BRINE UPON MINERAL SATURATION

As the solubility of some scale forming phases is pH dependent, the degree of degassing of the water with respect to $CO_2$ and $H_2S$ upon boiling affects its state of saturation with respect to these minerals. The degree of degassing is not quantitatively predictable. It is affected by various parameters, such as residence time in wellbores and surface equipment, the enthalpy of the fluid and the flow pattern of the two phases. The uncertainty in the degree of degassing of boiled geothermal water leads to a corresponding uncertainty in the calculated saturation index for minerals with pH-dependent solubility. Due to this uncertainty it is important to collect samples of water and steam from steam separators and from their analysis calculate gas partial pressures in both phases to reveal the extent of degassing. In steam samples, the gas mole fraction ($n^v_{gas}$) can be taken to be proportional to the gas partial pressure ($P_{gas}$), i.e. $P_{gas} = n^v_{gas} \cdot P_{total}$ . An aqueous speciation program is required to calculate gas partial pressures for the aqueous phase. In this connection it is also useful to calculate saturation indices for a variable degree of degassing to see how these two parameters are interrelated (Fig. 4).

If calculations of the type depicted in Fig. 4 show that saturation for some minerals is sensitive to the degree of degassing, mixing of condensate with the brine should be considered. Condensed steam is quite acid due to abundant carbon dioxide and hydrogen sulphide. Such mixing, thus, leads to a decrease in the water pH and in this way increases the solubility of minerals that have retrograde solubility in terms of pH, such as calcite and amorphous Mg-silicate. Mixing of condensate will, on the other hand, favour precipitation of other phases, such as amorphous aluminium hydroxide and also of amorphous silica, if the pH of the unmixed boiled geothermal water is high enough for appreciable ionization of the aqueous silica to occur and the mixing with the condensate decreases the pH sufficiently to convert this ionized silica to the unionized form. In order to assess the benefits of mixing condensate with boiled water, it is necessary to calculate the change in the saturation indices of all the potential scale forming phases as a function of the mixing ratio of the two aqueous phases.

## 5. EXAMPLES OF RESULTS

### 5.1 Momotombo, Nicaragua

At Momotombo, Nicaragua, part of the waste brine from the 70 MW power plant is injected at 4-5 bars vapour pressure (about 150°C) into two deep wells. Fig. 5 shows the calculated saturation index for calcite, amorphous silica and anhydrite for this brine as a function of temperature. In the range 115-160°C the brine is undersaturated with all these minerals. To avoid deposi-tion of these minerals in the injection wells, injection at 150°C is indeed favourable. If the water gains heat after leaving the injection well by contact with the hot reservoir rock, one would expect it to become calcite supersaturated soon. For that reason injection at a some-what lower temperature than 150°C would be optimal, at least, when considering the above mentioned minerals.

### 5.2 Krafla, Iceland

The power plant at Krafla, NE-Iceland, which has an installed capacity of 60 MW, has been in operation for a little over 20 years. So far the waste water, and the condensate from the cooling towers and the steam ejectors, have been disposed of on the surface. Plans are at present under way to dispose of the water and condensate by injection. One of the three wellfields at Krafla (Leirbotnar) has been divided into an upper sub-boiling reservoir and a deeper two phase reservoir. Formation of calcite scales has been troublesome in wells receiving water from aquifers in the upper sub-boiling reservoir. Scales which are composed of a mixture of oxides of silica, aluminium and iron, as well as sulphides, have been observed in some of the deeper wells in this wellfield. The intense formation of these scales has been linked with flux of magmatic gases from the intrusive heat source into the overlying geothermal system. Water and steam from individual wells in the Leirbotnar and Sudurhlídar wellfields is conveyed to a separator station close to the power plant (See Arnórsson, 1995 and Ármannsson et al., 1987 for detailed information on Krafla). The only productive well in the Hvíthólaklif wellfield, by the southern boundary of the Krafla geothermal system, has its own steam separator.

Fig. 6 depicts results for separated water from 5 Krafla wells (Nos. 5, 13, 15, 20 and 21) as a function of temperature. The dots indicate wellhead pressure for individual wells. For these calculations degassing was considered to be at maximum, i.e. corresponding to equilibrium distribution of the gases between the water and steam phases. The results in Fig. 6 show considerable variation between wells and that the water at wellhead conditions is undersaturated with respect to all the potential scale forming minerals, except calcite. Cooling of the waters makes them supersaturated with respect to amorphous silica but, with one exception, undersaturated with respect to calcite. For all of the wells the water is supersaturated with either silica or calcite, or both at all temperatures. If degassing were incomplete, or condensate mixed with the water to lower its pH calcite under-saturation could be attained for all the wells except No. 5, at temperatures of 150-200°C, thus making water from individual wells undersaturated with both calcite and amorphous silica in this range. Accordingly, appropriate mixing of separated water from each well with condensate and injection at about 150°C would prevent both calcite and amorphous silica scaling.

## 6 . PREVENTION OF AMORPHOUS SILICA SCALING BY RAPID COOLING

Deposition of quartz from supersaturated water in wellbores and surface pipeworks has not been reported. Silica scales only form if the geothermal water becomes amorphous silica supersaturated. Experimental work has demonstrated that the rate of equilibration between solution and quartz is very much temperature dependent (Morey et al., 1962, Rimstidt, 1997). Observations indicate that this is also the case with amorphous silica. Thus, appreciable deposition of amorphous silica is seen to occur from supersaturated water at relatively high temperatures (>90°C) whereas no observable deposition takes place when the same water has cooled down appreciably despite a higher degree of supersaturation. It appears that amorphous silica deposition from super-saturated geothermal water may be inhibited by rapid cooling. Experience in the Svartsengi geothermal field, Iceland, has demonstrated this. Here, brine (about seawater salinity) slightly undersaturated with respect to amorphous silica is conveyed from high pressure (6 bars abs.) steam separators to a low pressure separator (0.3 bars abs.) where the 160°C brine flashes to 70°C instantly. This rapid cooling suffices to quench the amorhous silica deposition reaction for all practical purposes. A technology that makes it possible to cool amorphous silica supersaturated geothermal water rapidly to inhibit scale formation would be very important for injection technology and exploitation of heat from such water. Experience at the Námafjall and Nesjavellir fields in Iceland, where the salinity of the geothermal water is very low, indicates that much cooling reduces amorphous silica deposition rates, even more than in the case of the brine at Svartsengi suggesting that the potential success of freezing this deposition reaction by rapid cooling depends on the water salinity.

A method which is known to retard amorphous silica deposition from supersaturated solution is to allow dissolved silica in excess of amorphous silica solubility to polymerize. This can be achieved by retention of the waste water in tanks or special conditioning ponds before injection. Treatment of this kind has been successful at Olkaria in Kenya for 20 years. Experimental work is very much needed to quantify the rate of amorphous silica deposition in terms of physical chemistry theory.

## 7. DISCUSSION

It is an expensive exercise to inject waste fluid from geothermal plants into wells to find out that scale formation deteriorates their performance, or even destroys them. It is inexpensive to assess thermodynamically mineral saturation for such waters as a function of temp-erature, boiling and degassing to find out if scale form-ation can be avoided by selecting the appropriate injection conditions. Chemical inhibitors have been successfully used to prevent calcite scaling. Descision on the use of inhibitors should be based on the thermodyna-mic assessment. It is of special interest to study inhibition of amorphous silica scale formation by quenching the deposition reaction by rapid cooling of the waste water to <50°C. Such technical solution would open up the possibility of utilizing heat from waste geothermal fluid before injecting it.

## REFERENCES

Ármannsson, H., Gudmundsson, Á., and Steingrímsson, B. (1987). Exploration and development of the Krafla geothermal area. *Jökull*, Vol. 37, pp. 13-29.

Arnórsson, S. (1981). Mineral deposition from Icelandic geothermal waters, environmental and utilization problems. *J. Petr. Techn.*, Vol. 33, pp. 181-187.

Arnórsson, S., and Stefánsson, A. (1999). Assessment of feldspar solubility constants in water in the range 0° to 350°C at vapor saturation pressures. *Am. J. Sci.,* Vol. 299, pp. 173-209.

Arnórsson, S., Sigurdsson, S., and Svavarsson, H. (1982). The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°. *Geochim. Cosmochim. Acta*, Vol. 46, pp. 1513-1532.

Bjarnason, J. O. (1994). The speciation program WATCH, version 2.1. National Energy Authority Report, 7 pp.

Gudmundsson, B. Th., and Arnórsson, S. (1999). Mineralfluid equilibria in the Krafla and Námafjall geothermal systems, Iceland. *Geochemistry of the Earth's Surface* (ed. H. Ármannsson), Balkema, Rotterdam, pp. 503-506.

Gunnarsson, I. (1999). Solubility experiments for amorphous silica and magnesium-silicate in hot water. Unpublished M.Sc. thesis, University of Iceland 74 pp.

Gunnarsson, I., and Arnórsson, S. (2000). Amorphous silica solubility and the thermodynamic properties of aqueous silica in the range 0-350°C. *Geochim. Cosmo-chim. Acta,* in press.

Kristmannsdóttir, H. (1989). Types of scaling occurring by geothermal utilization in Iceland. *Geothermics*, Vol. 18, pp. 183-190.

Morey, G.W., Fournier, R.O., and Rowe, J.J. (1962). The solubility of quartz in water in the temperature interval from 25 to 300°C. *Geochim. Cosmochim. Acta*, Vol. 26, pp. 1029-1043.

Naumov, G.B., Ryzhenko, B.N., and Khodakovsky, I.L. (1971). Handbook of thermodynamic data (translation of Russian report). U.S. Geol. Surv., Report WRD-74-001.

Reed, M.H. and Spycher, N. (1984). Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dil-ution. *Geochim. Cosmochim. Acta*, Vol. 48, pp. 1479-1492.

Rimstidt, J.D. (1997). Quartz solubility at low tempera-tures. *Geochim. Cosmochim. Acta*, Vol. 61, pp. 2553-56.

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Table 1. Solubility constants for some scale forming minerals.

| Mineral | logK(T) K |
|---|---|
| 1[a] | $-15.433-151.6/T-2.977\cdot10^{-6}\cdot T^{2}+5.464\cdot\log T$ |
| 2[b] | $10.22-0.0349\cdot T-2476/T$ |
| 3[c] | $78.414-3247.2/T-9.03\cdot10^{-6}T^{2}-28.723\cdot\log T$ |
| 4[d] | $-59.50+2398.4/T-0.4589\cdot10^{-3}T-0.554\cdot10^{-6}T^{2}+21.303\cdot\log T$ |
| 5[e] | $10.88+9355/T$ |

| | Mineral | Reaction |
|---|---|---|
| 1 | Am.silica | $SiO_{2,am}+2H_2O_{liq}=H_4SiO_4^{o}$ |
| 2 | Calcite | $CaCO_3=Ca^{+2}+CO_3^{-2}$ |
| 3 | Anhydrite | $CaSO_4=Ca^{+2}+SO_4^{-2}$ |
| 4 | Am. Al-hydroxide | $Al(OH)_{3,am}+OH^{-}=Al(OH)_4^{-}$ |
| 5 | Am. Mg-silicate | $Mg_4Si_3O_{10}+2H_2O+8H^{+}=4Mg^{+2}+3H_4SiO_4^{o}$ |

[a]Gunnarsson and Arnórsson (2000). [b]Arnórsson et al. (1982). [c]Gudmundsson and Arnórsson (1999). [d]This study. Based on data from Naumov et al. (1971) for the solid phase and on data for the aqueous species from Arnórsson and Stefánsson (1999). [e]Gunnarsson (1999).

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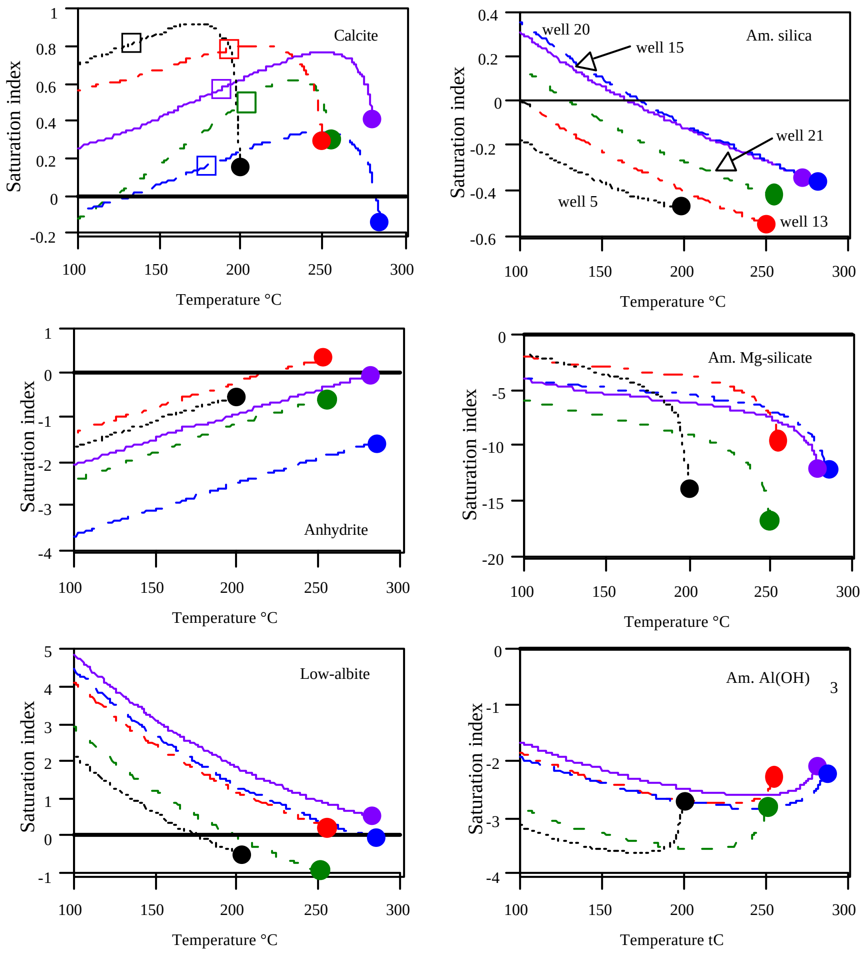

Figure 1. Changes in the saturation state for selected potential scale forming minerals during boiling of aquifer fluid feeding 5 wells at Krafla, Iceland. Dots: Aquifer water. Squares: Water at wellhead.

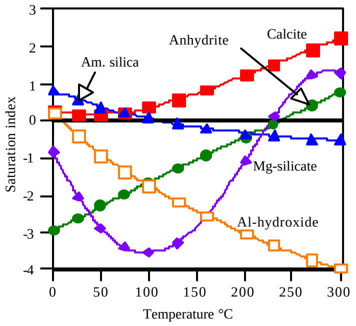

Figure 2. Mineral saturation in variably cooled and heated waters in the low-pressure steam separators at Krafla, Iceland.

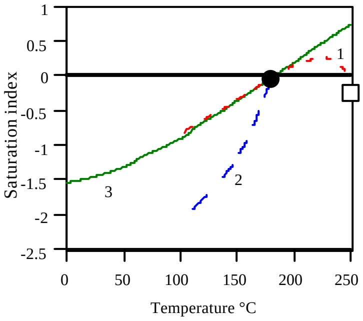

Figure 3. Calculated calcite saturation for water from well 1 at Amatitlan, Guatemala. 1: Adiabatic boiling and equilibrium degassing of the 250°C aquifer water (square). 2: Adiabatic boiling and equilibrium degassing of water separated at 180°C (10 bar abs. vapour pressure). 3: Cooling and heating of water separated at 180°C.

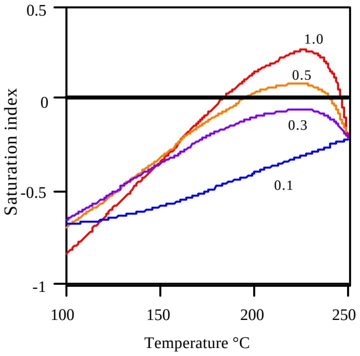

Figure 4. Calculated calcite saturation for boiled water from well 1 at Amatitlan, Guatemala, assuming variable degassing as indicated. The aquifer water is at 250°C and calculates to be slightly but insignificantly undersaturated.

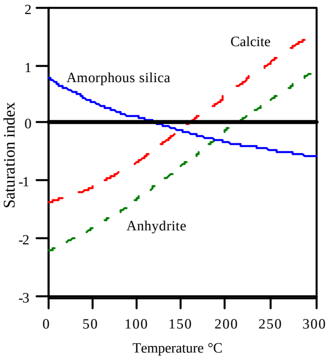

Figure 5. The state of anhydrite, calcite and amorphous silica saturation in brine injected into well RMT-18 at Momotombo as a function of temperature.

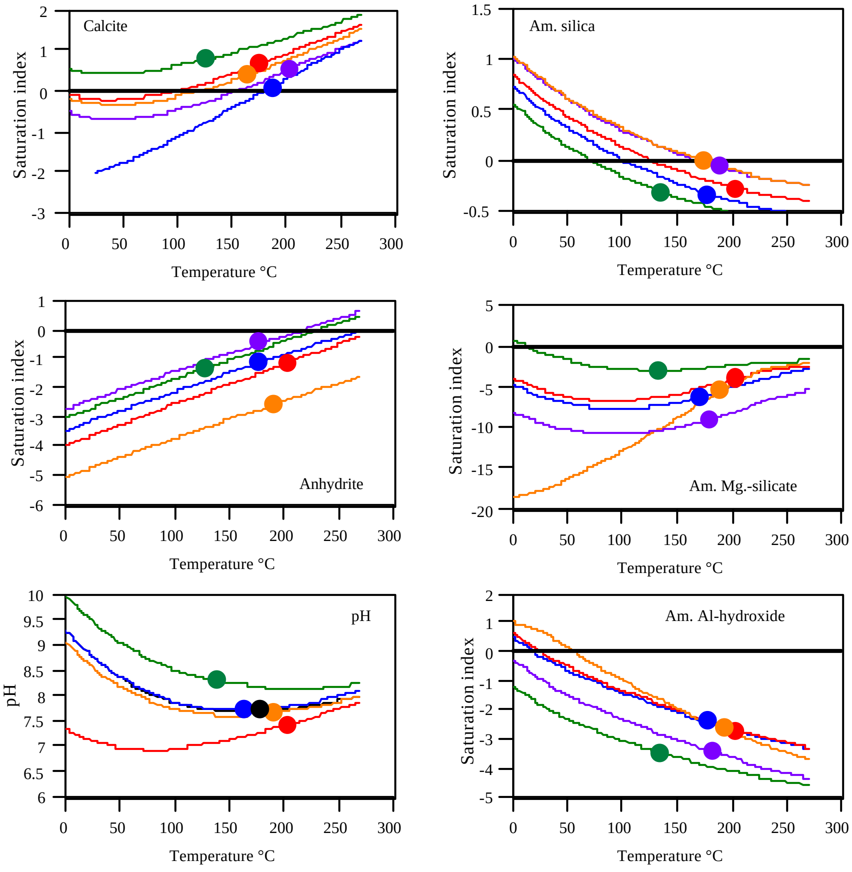

Figure 6. Saturation index for selected minerals and pH of separated water at wellhead pressure of 5 wells in the Krafla field, Iceland. Dots designate the wellhead temperature (pressure) for individual wells.