

Hydrochemistry in Geothermal Investigations in Iceland Techniques and Applications

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The role of hydrochemistry in geothermal exploration and development is described. During the surface exploration phase hydrochemistry is particularly useful in delineating regional ground-water movement, in estimating underground temperatures, and in mapping the areal extent of geothermal systems. From data obtained through exploratory and investigation, drilling hydrochemistry yields information on the direction of underground geothermal water flow, mixing processes, boiling in the aquifer, and distribution of underground temperatures. It also contributes significantly in defining and solving scaling and corrosion problems and is relevant for environmental aspects of fluid disposal and constructional design.

Introduction

About 30% of the energy consumption in Iceland comes from geothermal resources. So far the main use of geothermal energy has been for house heating. However, greenhouse farming based on geothermal heat is substantial and geothermal water and steam have been used on a small scale for industrial purposes. A 3 MW electric power plant has been in operation for 9 years at Námafjall in northern Iceland and a 60 MW plant is now under construction in the nearby Krafla geothermal field.

In all 25 district heating systems are in operation and another 2 are in the final

stages of construction and partly in operation, serving in all 36 communities. Additional 8 are in the planning stage. Presently close to 140,000 inhabitants, or 65% of the population, use geothermal energy for house heating. When the heating systems will be in operation that are now under construction and at an advanced planning stage, this figure will rise to 165,000 (76%). The peak load energy requirements for all the district heating services will then reach almost 600 MW thermal. Greenhouses cover about 140,000 square meters, requiring as a peak load about 40 MW thermal. Peak load requirements for various industrial uses amount to about 25 MW thermal, the most noteworthy being drying of diatomaceous earth with geothermal steam. A chemical plant, which will extract NaCl and KCl from geothermal sea-water, is now under construction at Reykjanes, southwest Iceland.

The process of exploring, developing and utilizing geothermal resources is conveniently divided into four phases: (1) a surface exploration phase, (2) an exploratory drilling phase, (3) an investigation drilling and testing phase, and (4) production drilling and production. Water chemistry, mingled with various other scientific and technological subjects is relevant for all these phases. It appears that a geochemist with a wide background in water chemistry can participate as an expert in a wider range of research topics than any other type of technical or scientific expert involved in geothermal research.

The boundaries between the four phases in development are not always clear. The results of the exploratory drilling may raise questions that demand further surface exploration. The exploratory drilling phase ends when the well data suffice for locating a potential production site. Investigation drilling aims then primarily at recovering fluid from the reservoir at this site and the testing of the investigation wells furnishes data for construction design and cost analysis. Production drilling involves further recovery of required fluid from the reservoir after decision has been taken to construct a geothermal plant. When a new well is sunk deeper than previous wells, this involves further exploration. The same holds, if a new well is located outside the previously drilled area, the definition of "outside" being dependent on the expert's understanding of existing reservoir data.

Many aspects of the role of geochemistry in geothermal exploration have been reviewed recently (White 1970, Ellis 1970, Truesdell 1975, Mahon 1975, Sigvaldason 1973, Fournier 1977, Ellis and Mahon 1977). The various research tasks involving water chemistry in geothermal development and utilization are summarized in Table 1. They are dealt with individually in the following chapters. The type of research and approach required at each development stage depends on the geological features of the area in question, the composition of the geothermal fluids and the type of use that is intended. These items should be borne in mind when transferring to other countries the experience obtained in Iceland of the application of hydrochemistry in geothermal development.

Hydrochemistry in Geothermal Investigations in Iceland

Table 1 - Tasks of hydrochemistry in geothermal exploration, development and utilization.

Phase in development	Individual tasks
Surface exploration	<ol style="list-style-type: none">1. Evaluate origin of water and direction of regional underground water flow.2. Estimate underground temperatures.3. Evaluate regional cold groundwater composition.4. Evaluate mixing with cold water in upflow zones.5. Map the extent of geothermal systems.6. Evaluate local direction of hot water flow.7. Characterize, as far as possible, reservoir water chemistry with respect to the intended utilization.8. Define, as far as water chemistry goes, potential environmental influence of utilization.9. Delineate a preliminary model of the geothermal system (together with the results of other investigations).
Exploratory drilling	<ol style="list-style-type: none">1. Assess reservoir water composition with reference to the intended utilization.2. Attempt to establish a quantitative understanding of the reservoir water composition through the study of mineral/solute equilibria.3. Estimate water temperatures at the point of well inflow.4. Evaluate, if boiling and phase separation in the reservoir affects the well discharge chemistry.5. Reevaluate direction of underground water flow.6. Define potential scaling and corrosion problems.7. Propose a model for the geothermal system.8. Revise potential environmental impact of the intended utilization.
Investigation drilling and testing	<ol style="list-style-type: none">1. Improve the results listed under items 1-5 in the exploration drilling stage.2. Establish changes (if any) in total well discharge composition that accompany long term well testing.3. Participate in scaling and corrosion tests which may include fluid transmission, fluid disposal and heat exchange.4. Participate in working out methods for disposal of waste fluids.5. Provide chemical data on fluid compositions relevant for construction design.6. Revise and refine reservoir model.
Production drilling and production	<ol style="list-style-type: none">1. Continue with research listed under items 2-6 in the investigation drilling and testing stage.2. Monitor the chemical composition of well discharges.

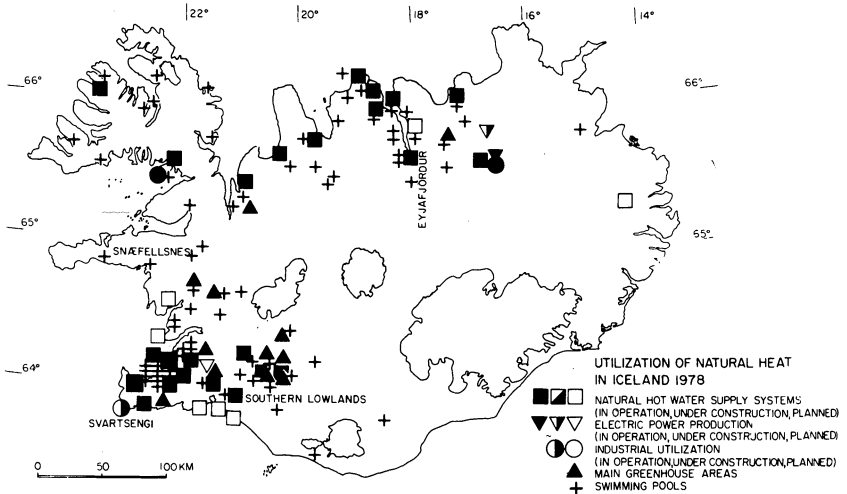


Fig. 1. Utilization of geothermal energy in Iceland.

Notes on Fluid Compositions and Water-Rock Equilibria

Geothermal waters in Iceland display large variations in their content of dissolved solids, or between 150 and 32,000 ppm. Analyses of representative waters are given in Table 2. They cover the known variation in temperature and salinity of geothermal waters in Iceland.

The most abundant components in the more dilute waters include silica and sodium and sometimes sulphate. With increasing salinity chloride along with sodium become the most abundant components. Waters in young and permeable rock formations near the coast tend to be highest in dissolved solids. It is considered that the increased salt content in these waters has been derived from sea-water, presumably by its percolation into the geothermal systems rather than by leaching from marine sediments (Pálmason et al. 1978).

Geothermal waters away from the coast and low in dissolved solids contain noteworthy low concentrations of chloride. This is considered to be due to low chloride content in the Icelandic basalts (see Sigvaldason and Óskarsson 1976). It appears that the mobility of all major dissolved components and protons in the geothermal reservoir waters, apart from chloride, are controlled by temperature dependent mineral/solute equilibria (Arnórsson et al. 1978, Pálmason et al. 1978). Similar results have been obtained for geothermal waters in other countries (Ellis 1970, Ellis and Mahon 1977). In upflow zones draining geothermal reservoirs, cooling, flashing and mixing with cold groundwater upsets the mineral/solute equilibria. Thus, the chemistry of geothermal waters emerging in springs may not be quantitatively explained in terms of such equilibria.

Table 2 - Composition (in ppm) of selected geothermal waters in Iceland giving an impression of the known range in temperature and salinity.^a

Location	Temp. °C	pH/°C	SiO ₂	Na	K	Ca	Mg	CO ₂	SO ₄	H ₂ S ^f	Cl	F	Diss. solids	Source
1. Geysir	84 ^b	8.7/84	509	209	22.4	0.8	0.03	135	114.5	0.7	122.0	11.5	1133	Arnórsson (1969)
2. Reykjaból, well 1	152 ^c	7.23/169 ^e	233	87.4	6.6	1.0	0.02	128	72.6	2.9	29.2	1.80	518	Arnórsson (1978a)
3. Brautarholt, well 1	72 ^b	9.71/20	70	149	3.2	17.6	0.07	10.3	77.4	<0.1	191.8	2.7	527	Arnórsson (1969)
4. Klausturhólar, well 1	103 ^{bd}	7.02/25	183	175	9.9	37.9	17.3	361	68.1	<0.1	95.3	0.89	814	NEA ^f
5. Seltjarnarnes, well 3	102 ^b	8.44/28	116	368	10.8	144.0	0.17	5.0	205.0	0.1	685.0	0.73	1631	Pálmarsson et al. (1978)
6. Svartsengi, well 4 ^h -g	243 ^c	6.08/240 ^e	461	6440	987	1053	1.14	539	35.5	5.8	12791	0.11	24006	NEA ^f
7. Reykjanes, well 8 ^a	292 ^c	5.58/246 ^e	501	9050	1271	1736	3.36	1234	68.5	20.6	19966	0.16	31572	Pálmarsson et al. (1978)
8. Lýshóll	57 ^b	6.72/19	219	452	34.2	86.8	20.7	1495	41.2	<0.1	80.0	5.00	1649	NEA ^f
9. Ólafsvík	5 ^b	4.54/21	10	12.2	2.2	3.9	4.15	1356	5.8	<0.1	22.3	0.06	53	NEA ^f
10. Laugaland, well LJ7	93 ^b	9.88/16	102	51.1	1.2	1.8	0.003	25.5	27.2	0.17	10.3	0.38	206	NEA ^f
11. Námafjall, well 10 ^a	300 ^c	7.31/272 ^e	607	118	22.8	0.5	0.02	23.2	26.6	232.0	82.3	0.75	1036	Pálmarsson et al. (1978)
12. Krafla, well 7 ^a	>342 ^{c-h}	6.88/248 ^e	172	60.6	11.3	0.7	0.01	36280	46.9	311.1	29.1	0.27	379	NEA ^f

^aCalculated composition of total well discharge. ^bMeasured temperature of discharge. ^cMaximum measured downhole temperature. ^dMaximum downhole temperature is 162°C. ^eComputed value for the total well discharge at the reported temperature which is the chalcodony/quartz equilibrium temperature. ^fUnpublished data of the National Energy Authority, Reykjavík. ^gAverage of 11 analyses collected in 1976 and 1977. ^hTemperature above the range of the instrument. ⁱTotal carbonate (H₂CO₃ + HCO₃⁻ + CO₃²⁻). ^jTotal sulphide (H₂S + HS⁻ + S²⁻).

The Surface Exploration Phase

Origin of Water, Regional Flow Pattern

The δD and $\delta O18$ content of the geothermal waters in Iceland indicate that they are for the most part meteoric in origin (Bödvarsson 1962, Árnason 1976, 1977a). However, the chloride and deuterium content of many thermal waters near the coast indicate the presence of a variably large sea-water component.

Deuterium has been extensively used in geothermal studies in Iceland as a tracer for the regional flow pattern of the geothermal water (Árnason 1976, 1977a) (Fig. 2). In general the regional flow pattern is from the interior of the country towards the coasts and relates to the topography. From estimation of the regional bedrock permeability and the distance between recharge and discharge areas, it has been concluded that the age of the thermal waters now appearing at the surface may be as much as 2,500-25,000 years (Árnason 1976, 1977a). Fridleifsson (1978) has pointed out that the regional flow pattern revealed by deuterium not only coincides with the topography but also with the direction of the regional strike. He considers that thick permeable beds of interstratified hyaloclastites may conduct the main water flow. It could, however, also be vertical permeable structures such as faults and dykes, but these structures run approximately parallel to the strike. The structural control of the regional underground water movement from the interior towards the coasts would explain the lack of geothermal activity in eastern Iceland. Here, in regional terms, the strike is roughly parallel to lines of equal altitude.

Estimation of Underground Temperatures

The chemical geothermometers that have been quantitatively calibrated have been used extensively in Iceland during the exploration phase in geothermal development. They include the silica, the Na-K and the Na-K-Ca geothermometers. These geothermometers give a semi-quantitative measure of water temperatures in geothermal reservoirs from chemical data of hot springs and shallow drillholes which issue water that has cooled on passage from the underground reservoir to the surface. The cooling may be conductive or result from steam formation. The application of these geothermometers involves correlation of the analyzed concentration of the respective constituents in the hot water with certain temperature dependent mineral equilibria. The following major assumption is involved: Equilibrium is attained in the geothermal reservoir between the respective dissolved constituents and a particular mineral and re-equilibration does not accompany cooling in the upflow zone.

During the last decade various gas and isotope equilibria have been used as quantitative geothermometers (see e.g. Ellis and Mahon 1977, Truesdell 1975, Árnason 1977b, Hulston 1977, McKenzie and Truesdell 1977, Panichi et al. 1977 and Sakai 1977). Apart from the hydrogen isotope geothermometer (Árnason

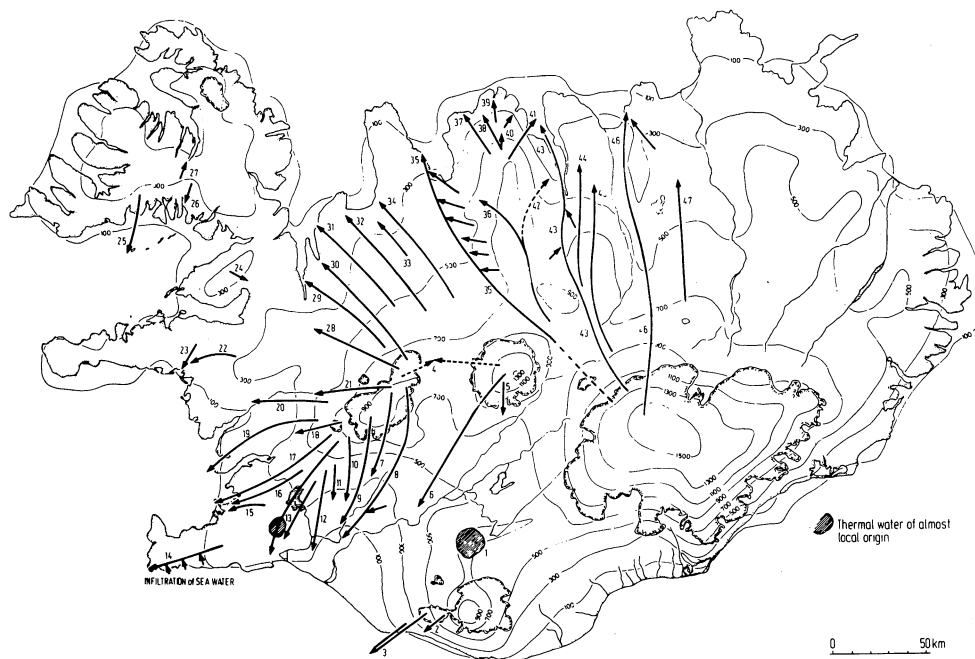


Fig. 2. Regional flow pattern of geothermal ground-waters in Iceland. Based on studies of hydrogen isotopes. Reproduced from Árnason (1976).

1977b) these geothermometers have been used very little in geothermal studies in Iceland and will be omitted in the present discussion.

The silica geothermometer is based on experimentally determined solubility of chalcedony (Fournier 1973) and quartz (Kennedy 1950, Morey et al. 1962). The concentration of the dissolved silica in the geothermal water is correlated with the solubility of these minerals and with the aid of the solubility curves the silica content of the water is related to the silica temperature. Equilibrium with chalcedony is assumed, if it yields values of less than 180°C. If higher temperatures are obtained, equilibrium with quartz is assumed (Arnórsson 1975). Truesdell (1975) and Fournier (1977) have given useful summaries of the silica and other geothermometers expressing the temperature dependence of the quartz and chalcedony solubilities in terms of simple equations (see Table 3).

An important fact that must be considered when applying the silica geothermometer is that equilibrium between mineral and solution involves only the unionized silica in solution. This is particularly significant for many of the dilute high pH geothermal waters in Iceland. The concentration of unionized silica in solution is obtained by subtracting the fraction which is ionized from the analyzed total silica content. This requires knowledge of the first ionization constant of silicic acid and an accurate measurement of the in-situ water pH, especially if its

Table 3 – Equations for chemical geothermometers.

1. Chalcedony (0-250°C) ^a	$t^{\circ}\text{C} = \frac{1032}{4.69 - \log \text{SiO}_2^1)} - 273.15$
2. Quartz (0-250°C) ^{a,f}	$t^{\circ}\text{C} = \frac{1309}{5.19 - \log \text{SiO}_2^1)} - 273.15$
3. Quartz (0-250°C) after steam loss ^a	$t^{\circ}\text{C} = \frac{1522}{5.75 - \log \text{SiO}_2^1)} - 273.15$
4. Na-K-Ca (4-340°C) ^b	$t^{\circ}\text{C} = \frac{1647}{\log(\text{Na}/\text{K})^2) + \beta^3) \log(\sqrt{\text{Ca}}/\text{Na})^2) + 2.24} - 273.15$
5. Na-K (100-275°C) ^c	$t^{\circ}\text{C} \equiv \frac{855.6}{\log(\text{Na}/\text{K})^2) + 0.8573} - 273.15$
6. Na-K (25-300°C) ^d	$\log \text{Na}/\text{K}^2) = -10.96 + 1709/\text{T}^{\circ}\text{K} + 3.18 \log \text{T}^{\circ}\text{K}$

The correction factor (I) recommended by Paçes (1975) for the Na-K-Ca geothermometer for water of less than 75°C with partial pressure of CO₂ above 10⁻⁴ atm. is:

$$I = 1.36 + 0.253 \log P_{\text{CO}_2}$$

This factor should be added to the term $\log(\text{Na}/\text{K}) + \beta \log(\sqrt{\text{Ca}}/\text{Na})$

The temperature dependence of the first ionization constant of silicic acid ($K_{\text{H}_4\text{SiO}_4}$) is described by the following equation where T is in °K.

$$\log K = -2.82 \cdot 10^3 / T + 2.78 \cdot 10^{-3} T - 1.87 \cdot 10^{-5} T^2$$

¹⁾in ppm ²⁾ in moles/kg ³⁾ $\beta = 4/3$ for $\sqrt{\text{Ca}}/\text{Na} > 1$ and $t < 100^{\circ}\text{C}$; $\beta = 1/3$ for $\sqrt{\text{Ca}}/\text{Na} < 1$ and $t > 100^{\circ}\text{C}$.

^aFrom Fournier (1977). ^bFrom Fournier and Truesdell (1973). ^cWhite and Ellis (1970), see Truesdell (1975). ^dBased on data from Helgason (1969) for equilibrium between Na- and K-feldspar and solution. ^eExtrapolated from the experimental data of Seward (1974). ^fThe following equation fits Kennedy's (1950) experimental data in the interval 200-370°C: SiO_2 (ppm) $\equiv 1.2 \cdot 10^{-4} t^{2.76} - 6.94 \cdot 10^{-24} t^{102}$ where t is in degrees centigrade (Hauksson pers. comm.).

value is above 9. The values of K_{diss} for silicic acid which are preferred have been found by extrapolation of the experimental data of Seward (1974) to low temperatures (Arnórsson unpublished work) (see Table 3).

Many hot spring waters have lost some steam during their passage to the surface. When so, it is necessary to correct for the increase in the silica concentration caused by the steam loss and possibly also for an increase in the water pH that has affected the relative concentrations of ionized and unionized silica. Such a pH increase results from degassing that accompanies the steam formation. In the case of hot springs in the high-temperature geothermal fields consideration of any pH changes can be omitted because it has been shown, even for the most dilute waters, that their pH is that low that practically all the dissolved silica is unionized. In reservoirs with dilute waters of less than 150-200°C, a significant fraction of the dissolved silica may, however, be ionized. In such cases precise estimation of the silica temperatures from the silica content of hot springs involves evaluation of the deep water pH as well as correlation for steam loss. Calculation of this deep water pH involves successive iterations taking into account the buffer action of the various weak acid equilibria (mostly silica, carbonic acid and hydrogen sulphide) assuming a certain amount of degassing to accompany the steam formation. A computer programme has been developed recently for such calculations (Arnórsson et al. unpublished work). Such tedious calculations can, however, be circumvented by the assumption that changes in water pH are only influenced by the buffer action of silica. This assumption holds within 5-10°C for all known water compositions and reservoir temperatures below 150-200°C whether or not steam loss has occurred underground. On the basis of this assumption the concentration of unionized silica in solution is found from measured water pH, analyzed total silica and the solution of the following equations, taking concentration [] to be equal to activity ():

$$\frac{(\text{H}_3\text{SiO}_4^-)}{(\text{H}_4\text{SiO}_4^0)} = \frac{K_{\text{diss}}}{(\text{H}^+)} \quad (1)$$

$$\text{SiO}_2(\text{analysed}) = [\text{H}_4\text{SiO}_4^0] + [\text{H}_3\text{SiO}_4^-] \quad (2)$$

The Na-K geothermometer is based on the temperature dependence of the partitioning of sodium and potassium between solution and alkali feldspars. Two calibration curves have been proposed for the Na-K geothermometer (see Truesdell 1975). These curves compare rather well, particularly at temperatures above about 150°C. Above about 150°C they fit well with the thermodynamic data presented by Helgeson (1969) describing equilibrium between alkali feldspars and solution (Fig. 3) but deviation increases with decreasing temperatures.

This geothermometer has been considered to be applicable only at temperatu-

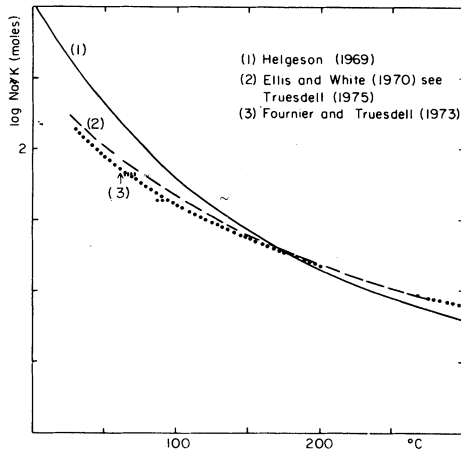


Fig. 3. Na/K ratios of waters in equilibrium with sodium and potassium feldspars.

res above 100°C because equilibrium between feldspar and solution may not be attained at lower temperatures (Ellis and Mahon 1977). Recent studies of water from deep wells in Iceland show, when applying data given by Helgeson (1969), that there is a good fit with Na-K ratios in the waters and the alkali feldspar equilibrium to temperatures as low as 30°C (Pálmason et al. 1978). This suggests that the Na-K geothermometer may be used at such low reservoir temperatures, if Helgeson's data are applied.

It has been observed that the Na-K geothermometer often yields anomalously high estimated temperatures when the water temperature is below 100°C or when the calcium content of the water is high. After careful examination of a wide range of geothermal water compositions and oil field waters Fournier and Truesdell (1973) proposed an empirical Na-K-Ca geothermometer. This geothermometer considered the partitioning of sodium, potassium as well as calcium in the relevant silicate exchange equilibrium.

Paçes (1975) has pointed out that cool (less than 75°C) carbon dioxide waters yield "unreasonably" high estimated temperatures and recommends a correction factor to be added to the expression for the Na-K-Ca geothermometer which is related to the carbon dioxide partial pressure (Table 3). Application of Paçes' correction factor yields anomalously low results (sometimes negative) for carbon dioxide waters in Iceland. It appears that the carbon dioxide bearing term of the correction factor does not affect so much the calculated Na-K-Ca temperature as does the value 1.36 (see Table 3). Accordingly, the data Paçes (1975) used to derive his correction factor may rather reflect a different stoichiometry for the relevant cation exchange reaction and not that the carbon dioxide content has a direct influence on the calcium concentration in the water, if chemical equilibrium is attained at these low temperatures.

Experience obtained through geothermal exploration work in Iceland indicates that the silica geothermometer is the most reliable of the chemical geothermometers. It may, however, yield high estimated temperatures for warm carbon dioxide waters. These waters have a rather low pH (5-7) so dissolution of the rock constituents may be sufficiently rapid to produce a solution that is maintained saturated with amorphous silica. Sluggish precipitation at the low temperature prevents formation of the more stable pure silica minerals, chalcedony and quartz.

Geothermal reservoir waters at 210°C become saturated with amorphous silica at 100°C through adiabatic cooling. Precipitation of this silica phase occurs easily with the effect that the silica content of hot springs tends not to indicate higher underground temperatures unless the water ascends very rapidly to the surface, or significant ionization of silica takes place as a result of degassing (increases pH) in the upflow zone. At these high temperatures the Na-K and Na-K-Ca geothermometers appear to be more reliable due to lesser rate of re-equilibration upon cooling (Ellis and Mahon 1977).

Groundwater Chemistry Characteristics

In geothermal exploration it is of major importance to establish the pattern of the groundwater chemistry in the respective area, whether or not surface thermal manifestations exist. This involves sampling and analyses of cold springs, wells, drillholes and surface waters. The pattern of the groundwater chemistry should be related with the geology and the topography of the area. Knowledge of the groundwater chemistry is essential for interpretation of resistivity surveying because the salt content of the water has a profound effect upon the bedrock resistivity. In upflow zones, tapping geothermal reservoirs, mixing of the geothermal water with local cold groundwater often occurs. For evaluation of such mixing on the geothermal water chemistry and the application of the chemical geothermometers, it is necessary to know the composition of the cold water component in the mixture.

Mixing in Upflow Zones

Many hot spring waters consist of a mixture of deep hot water and shallow cold water. The composition of the deep hot water component in the mixture must be evaluated for estimation of underground temperatures by the chemical geothermometers. Evaluation of mixing in upflow zones may also be useful in explaining variable chemistry and temperature of hot spring waters as has been demonstrated by Arnórsson (1975) for some thermal waters in the Southern Lowlands of Iceland. The study of the El Tatio geothermal field in northern Chile provides a classical example in this respect (Cusicanqui et al. 1975, Giggenbach 1978). Mixing models have been studied extensively by Truesdell and Fournier (1975) and Fournier (1977). In Iceland hot spring waters of mixed origin can often be

distinguished from unmixed geothermal waters by relatively low pH, low chloride but high sulphate (Arnórsson 1975).

Mixing on the boundaries of major upflow zones appears to be a common occurrence, e.g. in the Southern Lowlands of Iceland. This is reflected by centrally located hot springs with relatively high discharge rates surrounded by warm springs, which are often with insignificant flow. Mixing processes are also known in some of the high-temperature geothermal fields such as Krafla, Námafjall and Torfajökull. Here cooling caused by the mixing reduces or prevents underground boiling. This produces hot spring waters high in carbonate and often with relatively high sulphate (oxidation of sulphide) and calcium, but low pH (6-7).

If mixing takes place during horizontal movement of the hot water, aquifer temperatures encountered by drilling at the hot spring would at the most be equal to the temperature of the mixture and lower than that indicated by the chemical geothermometers. If, on the other hand, mixing takes place during vertical movement of the thermal water, a drillhole may penetrate the zone of mixing and subsequently strike aquifers hotter than indicated by direct application of the geothermometers on the mixed hot spring waters and presumably similar to that indicated when applying mixing models. A hydrochemical result which indicates mixing in upflow zones emphasizes evaluation of the hydrogeology of the area in question for successful siting of wells. Prior to drilling the hydrogeology could be revealed by geological mapping and by magnetic and resistivity surveys.

Mapping of the Extent of Geothermal Systems

Elements like chlorine, which are incompatible, i.e. they are not incorporated in geothermal minerals, may be used to map boundaries between geothermal systems or – to put it in another way – to map the areal extent of aquifers. Other incompatible elements in geothermal systems include boron, bromine, cesium and arsenic (Ellis and Mahon 1964, 1967). It is particularly convenient to use ratios of such elements to eliminate effects of mixing and boiling. In Iceland application of Cl/B ratios has proved useful.

The concentrations of incompatible elements in geothermal waters are controlled by the following factors:

- 1) their concentration in the rock
- 2) the contact area between water and rock
- 3) the proportion of water and rock in the geothermal system (porosity)
- 4) the flow rate through the system (permeability)
- 5) the duration of the geothermal activity
- 6) sources other than leaching such as juvenile or marine

The factors listed above are not necessarily independent. There appears often to be a rock-genetic relation between factors 1) to 4). Thus, it may be, eliminating other sources than leaching, that particular element ratios could be used as crude indicators of structural factors controlling permeability. A geothermal system defined by hydrochemical data is not necessarily identical to a system as defined by hydrological drillhole data.

It appears that fluorine concentrations in hot spring and drillhole waters, which have the same salinity, could be used to indicate zones of constant underground temperature, if below 100°C. In waters in basaltic rocks fluoride (F⁻) levels appear to be controlled by an ionic exchange reaction with OH⁻ (Pálmason et al. 1978). In waters below about 100°C far the greater part of the dissolved fluorine is as F⁻. Therefore total analyzed fluorine may be taken as F⁻. Cooling favours increase in the fluoride content of the water. As fluorine is a trace element in the basaltic rock, leaching accompanying cooling in upflow zones is limited and the fluorine content of hot springs will therefore be similar to that deep in the reservoir practically independent of cooling on passage to the surface.

Deuterium contents of hot waters have been used to distinguish waters of different hydrological systems. It is assumed that the deuterium content of the geothermal water is determined by the deuterium content of the precipitation in the recharge area. Different deuterium contents thus indicate different recharge areas and different paths of underground flow feeding the respective geothermal systems. In this way three geothermal fields have been recognised within the Reykjavík area (Árnason and Tómasson 1970). Similarly it has been demonstrated that three hydrological systems exist in the Hengill high-temperature area, southwest Iceland. There are two deep water systems feeding the wells at Nesjavellir and Hveragerdi respectively (originally thought to be one (Árnason et al. 1969)) and one shallow system which is of local meteoric origin and has a shallow circulation path (Fig. 4). The deep water systems have distant recharge areas to the northeast (Árnason 1976).

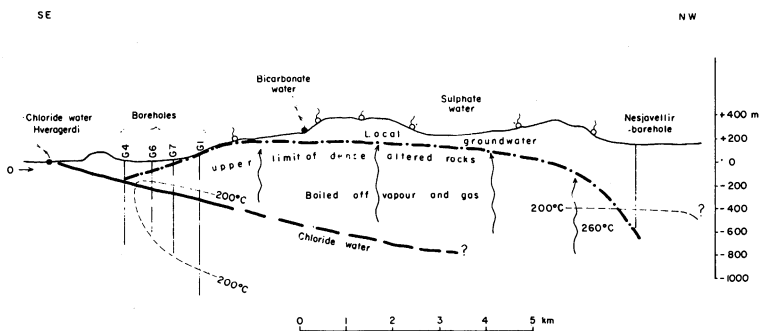


Fig. 4. A schematic hydrological cross section through the Hengill geothermal area in southwest Iceland based on the chloride and deuterium content of the water. Reproduced from Árnason et al. (1969).

Direction of Underground Water Flow

From the hydrochemical results on mixing and underground temperature conditions, one can infer about the movement of hot water underground. One should, however, be aware of the possibility that lateral variations revealed by surface exploration may be due to variable vertical gradients in isolated upflow zones and not horizontal. Early modelling of underground flow pattern should indeed make use of the hydrochemical results but it must include geological structures and hydrology.

Reservoir Water Chemistry – Environmental Influence – Modelling

Having estimated underground temperatures and evaluated possible effects of mixing and boiling in upflow zones, a characterization of the reservoir water chemistry should be delineated with respect to the intended utilization and potential environmental influence. Further, a preliminary model should be laid out based on the geochemical data and their interpretation. The model effectively summarizes the geochemical results used to site wells and should, of course, be incorporated with the results of other surveys into one model. Failure of putting all the results into one model calls for a critical review of the interpretation and possibly further data collection. It appears to be too common, when this kind of conflict arises, that the results of one or more of the exploration methods are ignored in decision making for exploratory drilling.

The Exploration Drilling Phase

If no surface thermal manifestations occur in an area subjected to geothermal exploration by drilling the hydrochemistry tasks linked to it involve those outlined in the previous and present sections. In the present phase it is particularly important to supplement the water chemistry data with downhole temperature measurements and geological logs including data on points of water inflow. Sampling should cover the discharge as well as downhole samples.

Assessment of Reservoir Water Composition and the Study of Mineral/Solute Equilibria

It is the task of the geochemist to provide data on the chemical composition of well discharges. In the case of hot-water wells this is usually straightforward, but data evaluation is more complex when dealing with wet-steam wells. Rather sophisticated sampling techniques are needed for collection of representative samples of the water and steam phases respectively. These techniques have been described by Mahon (1960), Ellis and Mahon (1977), Nehring and Truesdell (1977) and Arnórsson et al. (1978). For the calculation of the total well discharge composition, it is necessary to measure the enthalpy of the discharge and record the pressure at which the two phases are separated and collected.

The chemical components to be determined in the well fluid are related to the intended use and environmental aspects. Reliable values for many of the trace elements may be difficult to obtain because of contamination from the sampling and wellhead equipment. Some trace elements may also be precipitated to a significant extent during boiling, making it impossible to obtain values for their concentration in the unflashed reservoir water. Ellis and Mahon (1977) have given useful summaries of analytical techniques for many elements in geothermal fluids. Methods to calculate the composition of the total discharge of wet-steam wells from analyses of water and steam samples have also been given by Ellis and Mahon (1977) and Arnórsson et al. (1978).

It is often encountered that the chemical composition of individual well discharges varies considerably within a geothermal field and that this variation can be related to the aquifer depth and downhole temperatures. When so, it is particularly important to evaluate the influence of boiling, temperature dependent mineral equilibria, and mixing with shallow water upon the fluid composition and attempt to explain the observed chemical variation quantitatively in such terms. The results will provide a guideline in visualising how representative the exploratory well data would be for the field and what changes in well discharge chemistry might be expected in deeper wells.

Evaluation of chemical equilibria in geothermal systems is time consuming and complex and requires computer calculations. Programmes to serve this have been published (Truesdell and Singers 1974, Arnórsson et al. 1978).

Estimation of Well Inflow Temperatures

The chemical geothermometers discussed in the previous section may be applied to estimate temperatures of well inflow. In high-temperature geothermal fields re-equilibration is rather rapid below some 500 m where temperatures may be in excess of 250°C. For that reason the chemical geothermometers will yield estimated temperatures that approach those at the point of inflow. When boiling occurs in the aquifer the chemical geothermometers will usually yield values intermediate between those of the unflashed reservoir water and at the point of inflow because some precipitation or reaction with the rock takes place as the boiling water cools. When aquifers of different temperatures in the range 200-300°C feed the same well the silica geothermometer applied on the total well discharge gives the average temperature of the inflowing water within a few degrees because the quartz solubility curve is almost linear in this interval. A combination of downhole temperature measurements and chemical geothermometry may aid in locating points of major inflow into the well.

If the silica geothermometer indicates significantly lower temperatures than the cation exchange geothermometers, it is usually taken to indicate cooling in the feeding aquifer and underground temperatures will thus be higher than those measured at the point of inflow. The relative rate of re-equilibration upon cooling

for quartz and feldspar appears, however, to depend on water salinity. For very dilute waters (ionic strength less than 0.01) quartz precipitation appears to be more sluggish than at higher salinities so approximately equal shift will take place for the silica and cation exchange geothermometers as a result of cooling previously equilibrated reservoir water (Arnórsson 1977).

The pH of high-temperature reservoir waters (> 250°C) is always so low, even for the lowest salinities, that the dissolved silica is practically all unionized. The analyzed total silica may therefore be taken to represent unionized silica in estimating the silica temperature. This approximation is very handy, since it avoids calculation of reservoir water pH. Steam loss through evaporation in the well and in the feeding aquifer will increase the silica content in the aqueous phase. Such steam loss must be accounted for in estimation of silica temperatures. This is most conveniently done by assuming adiabatic single stage evaporation to the pressure of sampling. If a sample is collected at atmospheric pressure Eq. (3) in Table 3 may be applied. If the sample is collected at higher pressure, it is a good approximation to correct the analysed silica concentration for adiabatic single stage steam loss to 100°C with the aid of the following equations

$$h_s = h_{100} + X L_{100} \quad (3)$$

$$\frac{\text{SiO}_2(\text{anal.})}{1 - X} = \text{SiO}_2 \text{ (at 1 atm abs)} \quad (4)$$

and subsequent use of Eq. (3) in Table 3. h_s and h_{100} denote the enthalpies of the water at the sampling pressure and at 1 atmosphere abs. respectively, L_{100} is the latent heat of evaporation at 1 atmosphere abs. and X the fraction of water that has evaporated. The following assumption was made in deriving Eq. (3): $L_s = L_{100}$. At sampling pressure below 10 atm and reservoir temperatures above 200°C this assumption produces an error of less than 2°C.

Steam loss has no effect upon the Na-K geothermometer. The effect is non-significant for the Na-K-Ca geothermometer because the term $\sqrt{\text{Ca}/\text{Na}}$ makes a small contribution to $\log K$ (see Table 3) for all known natural waters above about 200°C.

Evaluation of Boiling and Phase Separation in the Aquifer upon Well Discharge Composition

The water and steam phases often separate partly as boiling occurs in aquifers feeding geothermal wells. The well discharge may thus not represent the chemical composition of the deep reservoir water.

Changes caused by phase separation in the aquifer can manifest themselves in changes in the enthalpy of the total well discharge and in its chemical composition. The latter may be partly due to steam enrichment or depletion in the discharge. It may, however, also result from reaction with the wall rock accompanying

adiabatic cooling in the aquifer. Steam enrichment or depletion both cause a lowering of the gas content of well discharges relative to the deep fluid composition.

During a 6 year observation period at Námafjall production wells have shown a pronounced decline in their silica content and an increase in Na/K ratios, both changes being due to reaction by the boiled and cooled water with the wall rock (Arnórsson 1977). At the same time the gas content of some of the well discharges has decreased. Comparable changes have been observed in geothermal fields outside Iceland, e.g. at Wairakei (Glover 1970).

Changes in well discharge chemistry with time may affect the magnitude of scaling problems and influence optimum construction design, e.g. as far as the gas content of steam is concerned. It is the task of hydrochemistry to evaluate the chemical results from exploratory wells with respect to any such changes. The evaluation mostly relies on resampling of the well discharge over a period of time and on hydrological and geophysical results that furnish data on underground boiling, and well discharge enthalpy.

Evaluation of the Direction of Underground Water Flow

Variations in the chemistry of well discharges can often be reliably used to deduce flow patterns in geothermal systems. The chemical geothermometers and gas concentrations are of particular importance in this respect. Highest geothermometry temperature is closest to upflow zones. Decrease in total gas content occurs as boiling and steam loss takes place in the formation. At the same time a change in gas ratios occurs, e.g. a decrease in $\text{CO}_2/\text{H}_2\text{S}$, due to their differential solubility in water. Flow is thus in the direction from high to low gas content and high to low $\text{CO}_2/\text{H}_2\text{S}$ ratios. Geothermometry has been used to locate upflow zones at Broadlands (Mahon and Ellis 1968) and variations in gas concentrations to path underground water movement at Námafjall (Arnórsson 1977) and at Wairakei (Glover 1970).

Scaling and Corrosion Problems

Troublesome scaling of calcite and silica is often associated with the utilization of high-temperature geothermal fluids. In one geothermal field, Krafla, severe scales of several iron bearing minerals have been encountered. These are considered to be of a rather special nature since they are connected with present magmatic activity in the area (Arnórsson 1979). Corrosion has been experienced in association with oxygen bearing waters of low temperatures ($< 80^\circ\text{C}$), carbon dioxide waters below 100°C and waters with rather high chloride. Scaling problems experienced in Iceland have been reviewed recently by Arnórsson (1979). Experience on corrosion has been summarized by Ragnars (1978) and Hermannsson (1970).

Formation of iron sulphides on the inside of pipelines occurs as a rule. It gives a

protective coating that hinders further reaction between pipewall and the geothermal fluid.

Knowledge of the physical and chemical conditions causing mineral deposition from geothermal waters allows an early evaluation of the magnitude of potential scaling problems and may aid in visualizing how they could be overcome. Deposition of silica in significant quantities only occurs if the geothermal water is cooled sufficiently to become supersaturated with amorphous silica. Geothermal reservoir waters equilibrate with quartz or chalcedony depending on temperature (Arnórsson 1975). Thus the temperature at which amorphous silica saturation is reached is directly related to well inflow temperatures. Through boiling of the geothermal water its pH may be raised sufficiently for significant ionization of the dissolved silica. Ionized silica does not participate in equilibrium with the solid phase. Therefore amorphous silica saturation temperatures may be lowered by pH increase caused by boiling. Separation of water and steam in an aquifer feeding a geothermal well may affect the degree of steam loss as pressure is decreased. The effects of all these processes on the temperature of amorphous silica saturation is demonstrated for specific cases in Fig. 5.

It has been observed that deposition of amorphous silica is accelerated by contact of the water with the atmosphere. This may be due to formation of minor amounts of ferric hydroxide which acts as silica nucleation sites.

Calcite scaling is associated with boiling and is always far the strongest at the first level of boiling (Arnórsson 1978a), but it has also been observed to be troublesome in the case of some high enthalpy well discharges (Ellis and Mahon 1977). Due to the control of temperature dependent mineral equilibria upon the chemistry of geothermal waters, the magnitude of calcite supersaturation caused

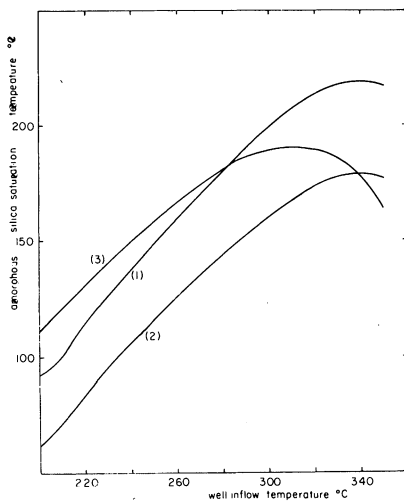


Fig. 5. Amorphous silica saturation temperatures in geothermal waters initially in equilibrium with quartz. One stage adiabatic boiling is assumed for (1) no ionization of dissolved silica upon boiling, (2) 1/3 ionization of the dissolved silica and (3) 80% excess steam in well discharge with an enthalpy corresponding with the inflow temperature and no silica ionization.

by boiling only depends on the salinity of the unboiled water and its temperature. Strongest supersaturation is produced at the lowest temperatures and at highest salinity (Arnórsson 1978a) (Fig. 6). Besides these effects the extent of degassing accompanying the steam formation affects the extent of calcite supersaturation produced. Calcite precipitation occurs easily from supersaturated solution. It is therefore expected that the rate of precipitation is principally governed by the degree of supersaturation caused by boiling. Mixing of calcite saturated waters of different temperatures and salinities may cause calcite precipitation.

An early evaluation of potential calcite scaling problems involves calculation of the calcium carbonate activity product for the geothermal water and subsequent derivation of the change in this activity product upon mixing and boiling. Changes which work in the direction of supersaturation favour scaling. Due to the temperature dependence of the chemical equilibria involved and complexing in aqueous solution, particularly at high temperatures, the calculations involve computer modelling. Methods that may solve calcite scaling problems have been summarized by Arnórsson (1979).

After the chemistry of exploratory geothermal wells has been presented and reviewed in terms of potential scaling and corrosion problems, tests should follow to work out the best available solution and demonstrate its reliance. The tests would be oriented by the geochemical results but would often be under the work of scope of chemical engineers. They could involve material selection, selection of operational wellhead pressures, methods of waste water treatment and disposal and even well spacing which influences drawdown in the reservoir around a group of wells.

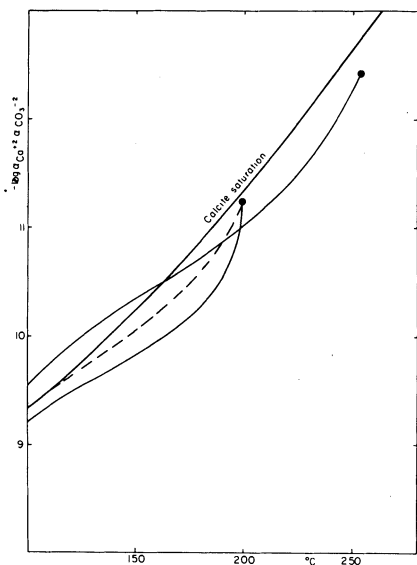


Fig. 6. Calcite supersaturation expressed in terms of $a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$, produced by single stage adiabatic boiling of selected geothermal waters. The solid lines indicate maximum degassing and the dashed line 1/5 of maximum degassing.

Modelling – Environmental Impact

The original model proposed on the basis of the surface exploration results should be reviewed in the light of the exploratory well data and a refined or a new model proposed. In this modelling hydrochemistry should contribute significantly to the evaluation of underground temperature distribution, direction of underground water flow and flashing in the aquifer. A more complete characterization of the reservoir fluid chemistry can now be made with respect to environmental aspects and the intended utilization. Here the geochemical data are relevant in laying out a test programme for methods of waste water disposal.

Investigation Drilling and Testing – Production Drilling and Production

The investigation drilling and testing phase is reached when a production site has been selected within the geothermal area, based on the exploratory drilling results. Now the scope of work of the hydrogeochemist and the chemical and mechanical engineers overlap. No new hydrochemical methods are involved in this phase. The study involves a continuation of the tasks initiated during the exploration drilling phase. It aims at defining and interpreting the fluid chemistry of the selected production site with respect to modelling, construction design and any scaling, corrosion and disposal problems.

When the geothermal reservoir is loaded during long term discharge of investigation wells, invasion of surrounding cold groundwater may occur. A change in the enthalpy of individual well discharges may also take place resulting from separation of water and steam during boiling in the aquifer. Both processes may influence the chemistry of the well discharge. The change may affect the magnitude of scaling and corrosion and affect optimum construction design. Any changes in well discharge chemistry will also be useful in modelling of the reservoir and in evaluating its response to exploitation. It is to be appreciated that many of the chemical changes, such as those caused by invasion of cold ground water, may appear before physical changes (pressure and temperature).

The end of the investigation drilling phase and the initiation of the production drilling phase is defined by the decision to construct a geothermal plant. Production drilling aims at recovering additional steam/water that may be required for the decided geothermal plant. Many of the hydrochemical changes that contribute to understanding the nature of the geothermal reservoir and its response to exploitation may not be apparent until after some years of production. In going from the investigation drilling and testing phase into production drilling and production no break is involved in the hydrochemical investigations. Continuity is to be emphasized.

Epilogue

Considerable capital investment is involved in the investigation drilling phase. This makes the economic people put a pressure to start production as soon as possible after this phase in development is initiated. The constraint thus brought about by the research and the economic points of view are probably best solved by a small scale production as a first stage, even using a transportable plant as suggested by Armstead et al. (1974), followed by gradual scaling up in production as experience is gained on the production characteristics of the geothermal reservoir.

It is always a matter of judgement when it is timely to decide to go ahead with the construction of a geothermal plant. Extreme cases can be mentioned. The Broadlands field in New Zealand has been proved by drilling to have an output in excess of 150 MW (Bolton 1975) and a 150 MW power plant is planned (Ellis and Mahon 1977). At Krafla, Iceland, it was decided to go ahead with constructional work before any steam was proved.

Geothermal exploration and development covers what might be called an "uncertainty project". This implies that considerable effort and investment is needed before 1) it is known if exploitation is beneficial and 2) a sound decision can be taken on production. The relevant energy authorities in many countries, who have gone into geothermal exploitation, have probably not had the painstaking experience of pathing their way through "uncertainty projects". They rest on precise planning of their energy budget based on reliable forecast of consumption and routine construction of conventional power plants. It is hoped that this article will be of some use in explaining how hydrogeochemistry, as one of many subjects involved in geothermal exploration and development, serves to cumulate data for a sound decision on exploitation. The approach described in this article is really one that involves minimum investment and maximum gain in information at each step or phase.

Examples of Hydrochemical Studies in Geothermal Development

The Southern Lowlands

The role of hydrochemistry in geothermal exploration, where surface thermal manifestations are abundant, is well illustrated by the work of Arnórsson (1970) and Stefánsson and Arnórsson (1975) in the Southern Lowlands of Iceland. The geothermal area is located in Quaternary basaltic lavas and hyaloclastites just east of the western active volcanic zone (Figs. 1 and 7). Acid rocks outcrop in the Geysir Area and near Flúdir. Surface thermal manifestations cover an area of some 1,000 km². Total flow from hot springs is about 330 l/sec. On the basis of the

**SOUTHERN LOWLANDS
HYDROTHERMAL SYSTEMS**

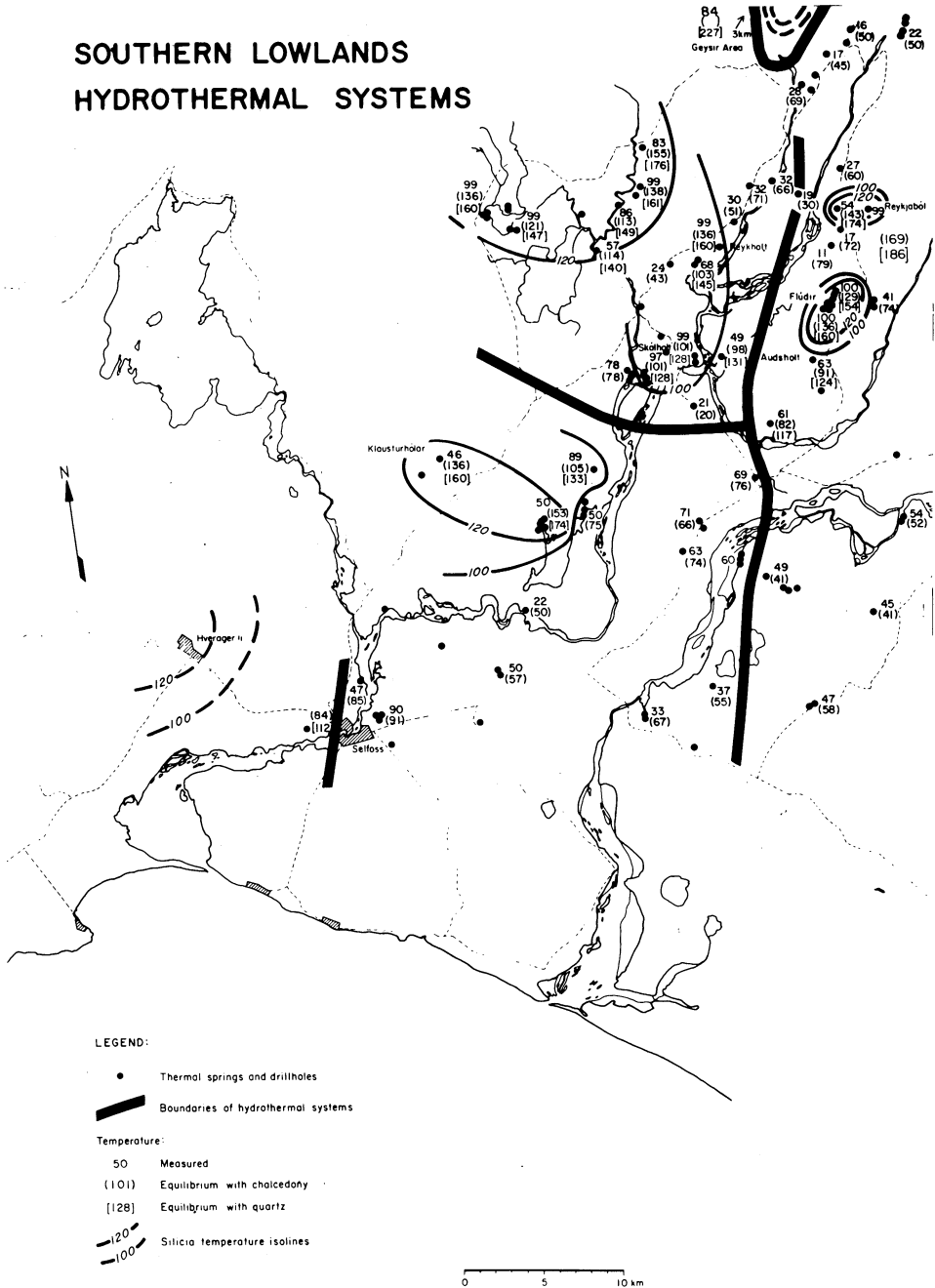


Fig. 7. Geothermal systems in the Southern Lowlands of Iceland as deduced from the C1/B content of the water. Silica temperature estimates are given for the majority of the hot springs and drillholes. From Stefánsson and Arnórsson (1975). Modified.

hydrochemical results alone, it was possible to delineate a model for the geothermal activity in the area.

The chloride/boron ratios of the thermal waters fall into 5 groups, geographically separated, suggesting the existence of 5 geothermal systems in the area (Fig. 7). On the whole there is a good conformity between estimated temperatures by the various chemical geothermometers (Table 4). They indicate subsurface temperatures of not less than 192-227°C in the Geysir Area. The other geothermal systems have lower estimated temperatures (Fig. 7). Within each of them the geothermometers indicate a regular geographic decrease in temperature from the maximum. The validity of the chemical geothermometer is demonstrated by the drilling results summarized below.

In 1974 one well was sunk to 850 meters depth about 2 km south of the main hot spring area at Geysir. The measured downhole temperature at 750 meters (deepest point of measurement) was 144°C and the gradient below the deepest inflow at 370 m was very close to 200°C/km. In 1972 wells were drilled to 700-800 m depth at Reykjaból and Reykholt. Water inflow temperatures, which are also maximum downhole temperatures, were 152°C and 133°C respectively, values which fit well with those predicted by the chemical geothermometers (Table 4, Fig. 7). A well was drilled to 1,100 m depth at Klausturhólar in 1977. Maximum temperature, which was at the bottom of the well, was 160°C. This result should be compared with the measured temperature in a nearby tepid spring of 46°C and the values estimated by the chemical geothermometers. The comparison shows that the water chemistry indicates high temperatures at depth despite conductive cooling in the upflow by some 100°C. A 630 m deep well was drilled by Audsholt in 1978. Water discharge temperature is 92°C and inflow occurs below 512 m. A non-flowing warm pool of 49°C is located near the well. Its chemistry indicated temperatures of 84-150°C (Table 4).

After the division of the geothermal activity in the Southern Lowlands into several systems was proposed on the basis of the hydrochemical results (Arnórsson 1970) resistivity surveying has been carried out in the area. The results of this survey conform remarkably well with the hydrochemical picture. They show bedrock resistivity lows coinciding with each of the geothermal systems as defined by the hydrochemistry and high resistivity zones on the boundaries between individual systems (Stefánsson and Arnórsson 1975).

Snæfellsnes

Two years ago geothermal exploration was initiated on the Snæfellsnes Peninsula in western Iceland, the aim of it and subsequent development being to provide several villages of 500-1400 inhabitants with geothermal water for house heating (Fig. 8). The results of this exploration are described in an unpublished report of the National Energy Authority (Jóhannesson et al. 1979). The geology of this area

Table 4 – Selected samples showing comparison between estimated temperatures by the chemical geothermometers.

Location	temperature °C						
	meas.	chalc.	quartz	Na-K-Ca	Na-K ^a	Na-K ^b	amorph. silica
Southern Lowlands:							
Geysir	84 ^c	–	227	192	195	234	
Reykholt, well 1	133 ^d	141	–	151	116	128	
Reykjaból, well 1	152 ^d	169	–	180	159	163	
Laugarvatn	99 ^c	132	–	146	122	132	
Laugarás	99 ^c	111	–	79	–	101	
Audshokt	49 ^c	98	–	84	145	150	
Brautarholt, well 1	72 ^c	77	–	69	–	89	
Klausturhólar, well 1	103 ^{c,e}	152	–	147	133	141	
Skammbeisstadir	45 ^c	52	–	86	–	85	
Laugaland, Holt, well 3	69 ^c	82	–	66	–	74	
Snæfellsnes:							
Lýsuhóll	57 ^c	165	–	170	160	163	62
Bergsholt	22 ^c	90	–	69	–	105	2
Ófærugil	19 ^c	121	–	26	–	66	26
Landbrotslaugar	54 ^c	134	–	62	–	74	37
Bjarnarfosskot	6 ^c	93	–	55 ^h	112	123	3
Ólafsvík	5 ^c	7	–	62 ^h	261	235	
Eyjafjörður:							
Laugaland LJ 7, discharge	93 ^c	88	–	79	–	94	
Laugaland LJ 7, 1360m ^f	91 ^g	87	–	78	–	97	
Laugaland LJ 8, 1800m ^f	96 ^g	90	–	71	–	100	
Björk	26 ^c	79	–	61	–	65	
Grýta	30 ^c	89	–	75	–	81	
Reykhúus	75 ^c	80	–	72	–	83	
Svartsengi:							
Well 3, discharge	229 ^d	–	232	244	240		
Well 4, discharge	243 ^d	–	240	243	239		

^aSee Eq. (5) in table 3. ^bSee Eq. (6) in table 3. ^cMeasured temperature of discharge.

^dMeasured maximum downhole temperature. ^eMaximum downhole temperature is 162°C.

^fDownhole samples from the reported depth. ^gMeasured temperatures at sampling points.

^hApplication of Paces (1975)-correction factor gave -14° and -7° respectively.

is relatively complex. Alkalic rocks are a characteristic feature. The area is volcanologically active but lies outside the main zones of volcanism and rifting. Volcanics from Tertiary to Recent age are exposed. Many dissected central volcanic complexes are known on the peninsula with intrusive complexes in their

core and intense hydrothermal alteration of the surrounding rock, bearing witness of ancient geothermal activity.

The surface thermal manifestations consist of several dispersed warm springs with a total discharge rate of less than 10 l/sec. Hydrochemically the area is noteworthy for its carbon dioxide springs some of which are thermal, but others are non-thermal. One of the main aims of the hydrochemical survey was to find out, if all the carbon dioxide waters were indicative of subsurface geothermal reservoirs.

The thermal carbon dioxide waters tend to show chemical features that fit with mineral equilibria at the temperature indicated by the chemical geothermometers. This is typical for geothermal reservoir waters in Iceland (Arnórsson et al. 1978, Pálmason et al. 1978). The large difference which is typically observed between measured and geochemical temperatures indicates strong conductive cooling in the upflow and therefore low permeability.

Contrary to the thermal waters the chemical composition of the non-thermal carbon dioxide springs indicates an overall non-equilibrium condition between water and rock. Some of the cold carbon dioxide springs show seasonal variation in temperature. These waters tend to be undersaturated with amorphous silica and calcite. Others which do not show seasonal temperature variations tend to be saturated with amorphous silica and calcite. Those waters showing the strongest temperature fluctuations are chemically almost identical to rain water to which carbon dioxide has been added.

All non-thermal carbon dioxide waters contain chloride concentrations similar to those of the precipitation whereas the thermal waters, especially on low ground near the coast contain much higher chloride concentrations (Fig. 8). High chloride concentrations are considered to be indicative of deep (long distance) ground-water circulation.

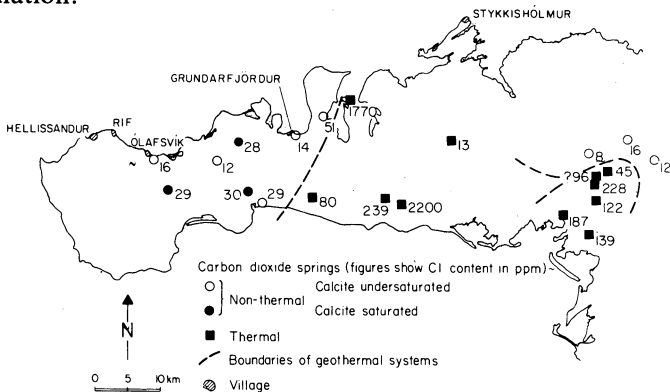


Fig. 8. The chloride content of carbon dioxide waters on the Snæfellsnes Peninsula, western Iceland. Division into hydrothermal systems is indicated as based on the chemistry of the waters.

On the basis of the temperature and the chemical features described above it was concluded that the non-thermal carbon dioxide waters do not indicate underground geothermal systems, but represent surface (seasonal temperature variation) or near surface waters (constant temperature) to which carbon dioxide has been added. It is thought that this carbon dioxide is of deep seated magmatic origin. The mechanism of its migration to the surface has not been studied.

For the thermal carbon dioxide waters there is often some discrepancy between the estimated temperatures by the different geothermometers. When so, the water tends to be saturated with amorphous silica at the temperature of the spring. The Na-K and Na-K-Ca geothermometers yield estimated temperatures similar to those measured in the spring but silica temperatures are higher. It may be that these warm waters do not equilibrate with chalcedony or quartz. The relatively low pH of the water may cause sufficiently rapid decay of the original rock constituents to maintain an amorphous silica saturated solution. This cannot, however, be the case for all warm carbon dioxide waters as the drilling results at Klausturhólar indicate, mentioned previously in the section on the Southern Lowlands. The control of the amorphous silica solubility on the mobility of dissolved silica should probably only be a suspect when warm waters are saturated with amorphous silica and the estimated silica temperature is much higher than the Na-K and Na-K-Ca temperatures.

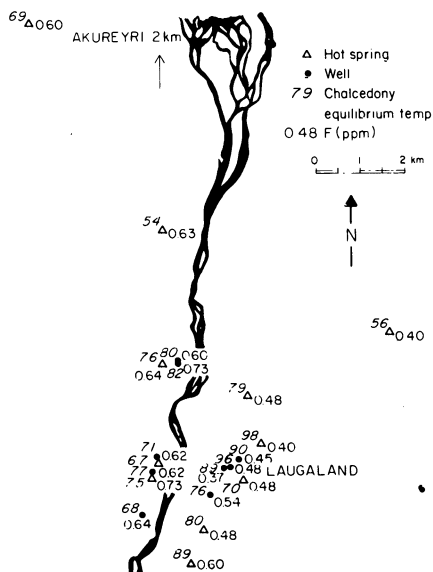
Eyjafjörður

This area is located in a monotonous pile of Middle Tertiary basalts in northern Iceland (Figs. 1 and 9). Warm and hot springs occur in many localities on either side of the Eyjafjörður valley. They tend to emerge at or near dykes. Total discharge is about 10 l/sec only. The general hydrological picture is that the Tertiary basalts have practically no permeability and underground flow of hot water is confined to near vertical dykes and faults.

Older chemical data of the thermal waters in the area indicated very homogeneous composition. It was therefore clear at the outset of the hydrochemical exploration summarized here (see Björnsson et al. 1978) that resampling was necessary for high precision analysis, if any chemical variations were to be detected in the water composition that could be used in estimating underground temperature variations and in modelling of the geothermal system. This reasoning was verified by the new analytical results. They showed on the whole smoother relationship between the various chemical parameters, e.g. good conformity in estimated temperatures by the various chemical geothermometers.

Six deep wells had been drilled at Laugaland (maximum depth 2,820 m) and one (1,306 m) at Grísará on the opposite side of the valley before the new hydrochemical survey was initiated. Maximum downhole temperatures are 96°C and 81°C respectively. Downhole sampling of the deep wells provided an excellent opportunity to compare the temperatures estimated on the downhole samples by

Hydrochemistry in Geothermal Investigations in Iceland



• Fig. 9. Estimated silica temperatures and the fluoride content of geothermal waters from springs and drillholes in Eyjafjörður, northern Iceland.

the chemical geothermometers with the directly measured temperatures deep in the reservoir. On average for 13 samples the chalcedony equilibrium temperature gave results that were 4°C below those measured in the deep wells at Laugaland. Corresponding figures for the Na-K-Ca and Na-K geothermometers (Helgeson's 1969 data, see Table 3) were 16°C and 4°C below and above measured temperatures respectively. The rather constant discrepancy between measured and Na-K-Ca temperatures suggests that this empirical geothermometer is not correctly calibrated, at least for the waters in question. The fit between measured and Na-K temperatures is remarkably good.

This year 2,1,100 and 1,480 m deep wells have been sunk at Tjarnir, about 2 km north of Laugaland. The temperature of a nearby spring is 26°C. The chemical geothermometers indicated, however, underground temperatures of 79°C (silica), 61°C (Na-K-Ca) and 67°C (Na-K). Recorded maximum downhole temperatures are 82°C and 80°C and discharge temperatures are 72°C and 70°C. Main inflow occurs at 475 and 940 m.

Chalcedony equilibrium temperatures are 70-98°C in the Laugaland area on the east side of the Eyjafjörður valley and 67-82°C on the west side (Fig. 9). Similar figures for the Na-K-Ca geothermometer are 53-75°C and 45-72°C and for the Na-K geothermometer 65-89°C and 57-83°C. Taking into account correction for the Na-K-Ca temperatures to fit those measured in the deep wells, it was concluded that underground temperatures are slightly higher on the east side of the valley than on the west side, or by 5-15°C. This temperature difference is significant because of the intended use of the hot water for house heating at Akureyri.

The concentrations of fluoride in thermal waters lie in the range of 0.30-0.55 and 0.60-0.65 ppm on the east and west side of the valley respectively (Fig. 9). Since these waters have very similar salinity it is expected, as previously discussed, that fluoride levels are controlled by temperature only. Fluoride concentrations tend to increase as temperatures decrease. Accordingly it was concluded that the distribution of fluoride in the geothermal waters in Eyjafjörður indicated higher temperatures in the east of the valley as compared with the west side, a result that supports the temperature estimates by the chemical geothermometers. It may be that each of the two exposed dyke swarms on either side of the valley represent a separate hydrological system with somewhat different reservoir temperatures.

Svartsengi

In 1972 two shallow wells (240 and 400 m) were drilled into the Svartsengi geothermal field in southwest Iceland with the aim of recovering hot water for space heating for the neighbouring village, Grindavík. Both wells proved to be good producers, but the water discharged was rather saline, about two-thirds the salinity of sea-water. It was obvious for that reason that the geothermal water could not be used directly for space heating. Transfer of the heat into water with a suitable composition was required. In early 1973 a feasibility report was submitted by the National Energy Authority, Reykjavík, which included plans for heat exchange tests and assumed that all the major towns and villages on the Reykjanes Peninsula would benefit from this geothermal utilization, including the NATO base at Keflavík (Björnsson and Ragnars 1973). The results of the heat exchange tests are described by Arnórsson and Sigurdsson (1974) and Arnórsson et al. (1975). They demonstrate well the use of hydrogeochemistry in identifying those factors that determine the quality of the heated water. The present summary of the Svartsengi project is intended to serve as an example for the benefit of linking geochemistry with chemical engineering in the more advanced stages of geothermal development.

Arnórsson and Sigurdsson (1974) showed that the quality of the heated water with respect to pH, free carbon dioxide and oxygen was not so much dependent on the gas content of the geothermal steam used, but mostly on the pH and the total carbonate of the water to be heated and the effectiveness of degassing during boiling of the heated water. Mostly on the basis of the geochemical tests it was recommended to heat the fresh cold water in two stages by low and high pressure geothermal steam and subsequent degassing by boiling in order to remove oxygen and lower carbon dioxide concentrations and raise the pH of the heated water. After further tests during the design stage for the plant it was decided not to mix the preheated water with high pressure steam. This steam contains a few thousand ppm of carbon dioxide. By indirect heating less reliance had to be placed on the degassing process, an advantage from an engineering point of view. Presently the cold fresh water for the plant is recovered from wells 3-4 km northwest of

Svartsengi and a fissure which is open down to the ground-water table.

Two deep wells (1,500 and 1,700 m) were drilled in 1974. Below some 700 m temperatures are very constant, or between 230°C and 243°C. Water at 243°C and in equilibrium with quartz becomes saturated with amorphous silica near 140°C (3.4 bars abs. saturated steam pressure) through one stage adiabatic boiling. Slight silica scaling was observed in a separator when run at a pressure close to the amorphous silica saturating point. It was therefore recommended to have operational separation pressure somewhat above that for amorphous silica saturation.

The relatively high salinity of the geothermal water has an accelerating effect upon amorphous silica deposition. However, the rate of deposition is not only dependent on water salinity but also on water temperature, pH and the degree of supersaturation (Arnórsson 1979). Scale formation was observed to diminish in the heat exchangers as the geothermal water became cooler despite the fact that the cooling caused the solution to become more supersaturated with amorphous silica.

In the low pressure separators, producing low pressure steam for preheating of the cold water, the geothermal brine becomes unavoidably highly supersaturated with amorphous silica. On the basis of the above mentioned results it was concluded that excessive cooling would mostly quench the deposition reaction, although it worked in the direction of increased supersaturation. Cooling by evaporation at low pressure improves the exploitation of the geothermal heat but it also raises constructional costs. Bearing these two factors in mind and potential silica deposition, it was decided to operate the low pressure separator at about 0.3 bars abs. (70°C saturated steam temperature).

The waste water at 70°C from the exchange plant at Svartsengi is discharged into the highly permeable lava fields west of the plant. However, mainly due to the high salinity of the water, it was expected during the design stage that deposition of amorphous silica was sufficiently rapid to clog infiltration channels, thus causing the infiltration pond to grow with time. One year of production has shown this to be the case. Two possibilities have been considered so far to solve this problem:

- 1) Allow the pond to grow in size until storage time is sufficient for deposition of all silica in excess of amorphous silica solubility and then infiltrate. Retention time of one week is thought to be sufficient.
- 2) Conduct the waste water in an open channel to the ocean (6 km). For economic reasons solution 1) is preferred.

As previously pointed out theoretical considerations indicated that deposition of calcite always occurs from geothermal waters when they boil and particularly at the point of first boiling. Downhole temperature and pressure measurements in the deep wells in Svartsengi shows that boiling sets in within the well at a depth of 400-500 m depending on wellhead pressure. It was thus expected that calcite deposition would be sufficiently rapid to clog wells and cleaning operations would

be necessary to restore well output. This was indeed experienced when one of the deep wells (No. 4) had been discharging for a period of 8 months in 1977. Suddenly the output fell and downhole measurements indicated scale of calcite at some 400 m. After drilling out the scale the well restored to its initial discharge rate. Since the calcite deposition is most severe at the point of first boiling and the cross sectional area of pores in the rock, even close to the well, far exceeds that of the well, it was thought that the calcite scaling problem might be eliminated by extending boiling into the aquifer. As discussed below the lower gas content of the shallow wells indicates boiling in the aquifer when they are not discharging. These results favour thus that the heaviest calcite deposition occurs in the aquifer and not in the well. Downhole temperature measurements in the shallow wells during discharge indicate boiling in the aquifer. Now, one of the shallow wells (No. 3) has been blowing continuously since December 1977 and there is no sign of any drastic decline in the flow rate (written in Dec. 1978). If longer term tests are positive an obvious attempt to circumvent the calcite scaling problem is by drilling of shallow wells.

The shallow wells in Svartsengi contain about 5 times less total carbonate than the deep wells (Fig. 10). Below 700 and 900 m the temperature in the deep wells is 240-243°C. Bottom hole temperature in the deeper of the shallow wells (350 m) is 229°C. The difference in the carbonate content between the deep and the shallow wells cannot be explained by conductive cooling. Assuming one stage adiabatic boiling, subsequent removal of the steam and maximum degassing this difference would correspond to 2-3% steam loss (Fig. 10) and more, if degassing was not complete, e.g. 8% in the case of 1/5 maximum degassing. The relatively slow ascend of the fluid through the rock as estimated from calculated permeability (Eliásson pers.comm.) would favour approach towards maximum degassing. A

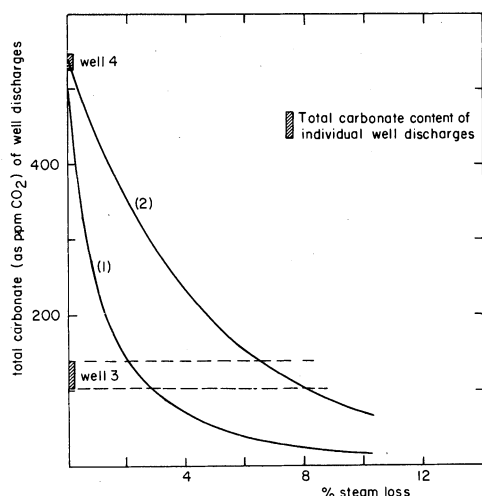


Fig. 10. The total carbonate content of boiled and non-boiled geothermal water feeding drillholes in Svartsengi. The curves show the total carbonate content of water, originally at 243°C and with 545 ppm of total carbonate (calculated as CO₂), after steam loss through one stage adiabatic boiling for (1) maximum degassing and (2) 1/5 of maximum degassing.

temperature drop from 243°C to 229°C corresponds to steam loss of 3.7% for one stage adiabatic flashing (Fig. 10).

The calculated temperature of equilibrium with quartz from the analysed silica content of the water fits well with the measured maximum downhole temperatures in the deep and shallow wells respectively. For well 3 it is 232°C as compared with the measured value of 229°C. For well 4 the same figures are 240°C and 243°C. Na-K-Ca and Na-K temperatures are, however, the same in both wells or 244°C and 240°C in well 3 and 243°C and 240°C in well 4 (Arnórsson 1978c). Salinity differences are not observable so it seems unlikely that mixing with cold fresh water could account for the temperature differences between the deep and shallow wells. Since it is expected that re-equilibration is slower for the ionic exchange geothermometers than silica the discrepancy in the shallow well No. 3 is taken to indicate that cooling of the deeper water has occurred during ascent and that deposition of silica accompanied this cooling.

The chemical data and results presented above (the gas content of the wells and the results for the chemical geothermometers) have provided useful information for hydrological modelling of the Svartsengi geothermal system (Elíasson et al. 1977).

References

- Armstead, H. C. H., Gorhan, H. L., and Mueller, H. (1974) Systematic approach to geothermal development. *Geothermics*, 3, 41-52.
- Árnason, B. (1976) Groundwater systems in Iceland traced by deuterium. *Societas Scientiarum Islandica*, XLII, Reykjavík.
- Árnason, B. (1977a) Hydrothermal systems in Iceland traced by deuterium. *Geothermics*, 5, 125-151.
- Árnason, B. (1977b) The hydrogen-water isotope thermometer applied to geothermal areas in Iceland. *Geothermics*, 5, 75-80.
- Árnason, B., Theodórsson, P., Björnsson, S., and Sæmundsson, K. (1969) Hengill, a high temperature area in Iceland. *Bull. Volcanologique*, Tome XXXIII - 1, 245-260.
- Árnason, B., and Tómasson, J. (1970) Deuterium and chloride in geothermal studies in Iceland. *Geothermics, special issue 2*, 2, Part 2, 1405-1415.
- Arnórsson, S. (1969) A geochemical study of selected elements in thermal waters of Iceland. An unpublished Ph. D. thesis, Univ. of London.
- Arnórsson, S. (1970) Geochemical studies of thermal waters in the southern lowlands of Iceland. *Geothermics, special issue 2*, 2, Part 1, 547-552.
- Arnórsson, S. (1975) Application of the silica geothermometer in low-temperature hydrothermal areas in Iceland. *Am. J. Sci.*, 275, 763-784.
- Arnórsson, S. (1977) Changes in the chemistry of water and steam discharged from wells in the Námafjall geothermal field, Iceland, during the period 1970-76. *Jökull*, 27, 47-59.

- Arnórsson, S. (1978a) Precipitation of calcite from flashed geothermal waters in Iceland. *Contrib. Mineral. Petrol.*, 66, 21-28.
- Arnórsson, S. (1978b) Major element chemistry of the geothermal sea-water at Reykjanes and Svartsengi, Iceland. *Min. Mag.*, 42, 209-220.
- Arnórsson, S. (1978c) Progress report on the results of chemical analysis of geothermal water and heated water in the power plant of Hitaveita Sudurnesja in Svartsengi. National Energy Authority report no. JHD 7836. In Icelandic.
- Arnórsson, S. (1979) Mineral deposition from Icelandic geothermal waters: Environmental and utilization problems. Proceedings of the SPE Symposium on Oilfield and Geothermal Chemistry, Houston, 22-24 Jan., 1979, 267-274.
- Arnórsson, S., and Sigurdsson, S. (1974) The utility of waters from the high-temperature areas in Iceland for space heating as determined by their chemical composition. *Geothermics*, 3, 127-141.
- Arnórsson, S., Ragnars, K., Benediktsson, S., Gíslason, G., Thórhallsson, S., Björnsson, S., Grönvold, K., and Línal, B. (1975) Exploitation of saline high-temperature water for space heating. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 3, 2077-2082.
- Arnórsson, S., Grönvold, K., and Sigurdsson, S. (1978) Aquifer chemistry of four high-temperature geothermal systems in Iceland. *Geochim. Cosmochim. Acta*, 42, 523-536.
- Björnsson, S., and Ragnars, K. (1973) District heating supply from Svartsengi. An unpublished report of the National Energy Authority, Reykjavík. (In Icelandic).
- Björnsson, A., Sæmundsson, K., Einarsson, S., Thórarinnsson, F., Arnórsson, S., Kristmannsdóttir, H., Gudmundsson, Á., Steingrímsson, B., and Thorsteinsson, Th. (1978) Geothermal exploration in Eyjafjörður, progress report, National Energy Authority report no. JHD 7827. In Icelandic.
- Bolton, R. S. (1975) Recent developments and future prospects for geothermal energy in New Zealand. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 1, 37-42.
- Bödvarsson, G. (1962) The use of isotopes of hydrogen and oxygen for hydrological purposes in Iceland. *Jökull*, 12, 49-54.
- Cusicanqui, H., Mahon, W. A. J., and Ellis, A. J. (1975) The geochemistry of the El Tatio geothermal field, northern Chile. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 1, 703-711.
- Eliásson, J., Arnalds, S. S., and Kjaran, S. P. (1977) Svartsengi: Hydrological study of the geothermal system. National Energy Authority report no. SFS 7702.
- Ellis, A. J. (1970) Quantitative interpretation of chemical characteristics of hydrothermal systems. *Geothermics, special issue 2*, 2, Part 1, 516-528.
- Ellis, A. J., and Mahon, W. A. J. (1964) Natural hydrothermal systems and experimental hot-water-rock interactions. *Geochim. Cosmochim. Acta*, 28, 1323-1357.
- Ellis, A. J., and Mahon, W. A. J. (1967) Natural hydrothermal systems and experimental hot-water – rock interactions – II. *Geochim. Cosmochim. Acta*, 31, 519-531.
- Ellis, A. J., and Mahon, W. A. J. (1977) *Chemistry and geothermal systems*. Academic Press, New York, 392 p.

Hydrochemistry in Geothermal Investigations in Iceland

- Fournier, R. O. (1973) Silica in thermal waters: laboratory and field investigations. Proceedings of the International Symposium on Hydrogeochemistry and Biochemistry, Japan, 122-139.
- Fournier, R. O. (1977) Chemical geothermometers and mixing models for geothermal systems. *Geothermics*, 5, 41-50.
- Fournier, R. O. and Truesdell, A. H. (1973) An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, 37, 1255-1275.
- Fridleifsson, I. B. (1978) Applied volcanology in geothermal exploration in Iceland. *Pure Applied Geophys.*, 117 (in press).
- Giggenbach, W. F. (1978) The isotopic composition of waters from the El Tatio geothermal field, northern Chile. *Geochim. Cosmochim. Acta*, 42, 979-988.
- Glover, R. B. (1970) Interpretation of gas compositions from the Wairakei field over 10 years. *Geothermics, special issue 2*, 2, 1355-1366.
- Helgeson, H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.*, 267, 729-804.
- Hermannsson, S. (1970) Corrosion of metals and the forming of a protective coating on the inside of pipes carrying thermal waters used by the Reykjavik Municipal District Heating Service. *Geothermics, special issue 2*, 2, 1602-1612.
- Hulston, J. R. (1977) Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand. *Geothermics*, 5, 89-96.
- Jóhannesson, H., Thórarinnsson, F., Arnórsson, S., Benjamínsson, J., and Ármannsson, H. (1979) Geothermal exploration on Snæfellsnes. National Energy Authority report (in preparation).
- Kennedy, G. C. (1950) A portion of the system silica-water. *Econ. Geol.*, 45, 629-653.
- Mahon, W. A. J. (1960) Sampling of geothermal drillhole discharges at Wairakei, New Zealand. Proceedings of the U.N. Conference on New Sources of Energy, Rome 1960, paper E/35/9/46.
- Mahon, W. A. J. (1975) Review of hydrogeochemistry of geothermal systems = prospecting, development, and use. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 1, 775-783.
- Mahon, W. A. J., and Ellis, A. J. (1968) The chemistry of the Broadlands geothermal field. In Report on Geothermal Survey at Broadlands, Department of Scientific and Industrial Research, New Zealand, Geothermal Report no. 5, 116.
- McKenzie, W. F., and Truesdell, A. H. (1977) Geothermal reservoir temperatures estimated from the oxygen isotope compositions of dissolved sulfate and water from hot springs and shallow drillholes. *Geothermics*, 5, 51-62.
- 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*, 26, 1029-1043.
- Nehring, N. L., and Truesdell, A. H. (1977) Collection of chemical, isotope, and gas samples from geothermal wells. Proceedings, Second Workshop on Sampling and Analyses of Geothermal Effluents, Las Vegas, February 1977.
- Paçes, T. (1975) A systematic deviation from the Na-K-Ca geothermometer below 75°C and above 10^{-4} atm P_{CO_2} . *Geochim. Cosmochim. Acta*, 39, 541-544.
- Pálmason, G., Arnórsson, S., Fridleifsson, I. B., Kristmannsdóttir, H. Sæmundsson, K.,

- Stefánsson, V., Steingrímsson, B., and Tómasson, J. (1978) The Iceland crust: evidence from drillhole data on structure and processes. Proceedings of the Second Maurice Ewing Symposium: Indications of Deep Drilling Results in the Atlantic Ocean, Argon House, Tuxedo, New York.
- Panichi, C., Ferrara, G. C., and Gonfiantini, R. (1977) Isotope geothermometry in the Larderello geothermal field. *Geothermics*, 5, 81-88.
- Ragnars, K. (1978) Methods of exploration and exploitation of low-temperature geothermal fields in Iceland. National Energy Authority report no. JHD 7833.
- Sakai, H. (1977) Sulfate-water isotope thermometry applied to geothermal systems. *Geothermics*, 5, 64-74.
- Seward, T. M. (1974) Determination of the first ionization constant of silicic acid from quartz solubility and borate buffer solutions to 350°C. *Geochim. Cosmochim. Acta*, 38, 1651-1664.
- Sigvaldason, G. E. (1973) Geochemical methods in geothermal exploration. In Geothermal Energy, Unesco Paris, pp. 49-59.
- Sigvaldason, G. E., and Óskarsson, N. (1976) Chlorine in basalts from Iceland. *Geochim. Cosmochim. Acta*, 40, 777-789.
- Stefánsson, V., and Arnórsson, S. (1975) A comparative study of hot-water chemistry and bedrock resistivity in the southern lowlands of Iceland. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 2, 1207-1216.
- Truesdell, A. H. (1975) Geochemical techniques in exploration, summary of section III. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 1, 53-79.
- Truesdell, A. H., and Singers, W. (1974) The calculation of aquifer chemistry in hot-water geothermal systems, *Jour. Res. U. S. Geol. Survey*, 2, 271-278.
- Truesdell, A. H., and Fournier, R. O. (1975) Calculations of deep temperatures in geothermal systems from the chemistry of boiling spring waters of mixed origin. Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources, San Francisco 20-29 May 1975, 1, 837-844.
- White, D. E. (1970) Geochemistry applied to the discovery, evaluation, and exploitation of geothermal energy resources: rapporteur's report. *Geothermics, special issue 2*, 1, Part 1, 58-80.

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