



ASSESSMENT OF PRODUCTION CHARACTERISTICS OF GEOTHERMAL FLUIDS AND MONITORING OF CORROSION AND SCALING ORADEA, ROMANIA AND SELTJARNARNES, ICELAND

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ABSTRACT

Data from a few Romanian geothermal fields were reviewed and production characteristics of the geothermal fluids assessed. Scaling and corrosion problems in a Romanian geothermal fields were studied and compared with an Icelandic geothermal field. Emphasis was placed on the geothermal fields of Oradea and Borş. For comparison, the Icelandic geothermal field Seltjarnarnes was chosen. Severe scaling problems are not expected in Oradea, but in Borş they have been encountered. Similarly, corrosion problems have appeared in Borş due to high salinity of the thermal fluid, but inhibitors are used to prevent it. Regular chemical monitoring is suggested to be able to see, as soon as possible, chemical changes that may later lead to scaling or corrosion. Also, the installation of scaling/corrosion device at wellheads is suggested. Comparison of chemical analysis in the Seltjarnarnes field shows considerable changes with time, mainly due to infiltration of seawater in the top of the reservoir, but also due to mixing of aquifers of different temperatures. A scaling/corrosion device was installed into well SN-04 and observed for four weeks. A thermowell that been in SN-04 for several years was analysed, showing minor traces of scaling and corrosion.

1. INTRODUCTION

The main aim of this study was to appreciate the need for chemical monitoring and predict possible corrosion and scaling during production in some Romanian geothermal fields. The fields chosen for this study are the Oradea and Borş reservoirs, described in detail in Chapter 5. Also the author received training in the use of corrosion and scaling test devices and analytical methods to be later installed in Romania.

The geothermal fields near Oradea were especially studied. The chemical composition of the fluids in Oradea and Borş is very different. The temperature of the fluid in Borş is also higher than in Oradea. Wellhead temperatures are 70-105°C in Oradea and around 115°C in Borş. The WATCH program was

used to study the behaviour of the geothermal fluid during exploitation time in several selected Romanian wells and make predictions about calcite scaling. The Seltjarnarnes field, a low-temperature geothermal reservoir in Iceland, was studied for comparison where corrosion problems have been experienced and calcite scaling is anticipated. Complete chemical analysis was made of geothermal water from two wells, SN-4 and SN-12. Analysis of a corroded thermowell (protection tube for thermometer) from well SN-4 was made. The WATCH program was used to model what happens in geothermal fluids under different conditions, first at reservoir temperature and then during water influx into the plant and distribution system during production.

2. PREDICTION OF SCALING AND CORROSION

Calcium carbonate is the most common scaling in geothermal production systems utilizing water of low and medium temperature, but silicates and metallic sulphides and oxides may also be precipitated. The potential scaling problems of a geothermal utilization depend both on the type of water and the treatment of the water (Thorhallsson, 1996). Therefore, a reliable analysis of the water and a simulation of the changes occurring during the intended utilization are needed to predict possible scaling. Major problems have arisen in a few hitaveitas (municipal heating services) due to calcium carbonate scaling (Kristmannsdóttir, 1989). In all of them, either the water temperature was relatively low (about 60°C) and the water brackish or mixing has occurred between water of different temperatures and salinity.

Dissolved oxygen and free CO₂ in geothermal water is extremely corrosive to steel pipes. The corroded pipe surfaces will also accelerate the precipitation of calcium carbonate from the water. Geothermal waters frequently contain hydrogen sulfide, which will react with any oxygen taken up in storage tanks and through plastic pipes and, thus, act as an inbuilt inhibitor for the corrosion of steel equipment. Some of the waters are free of hydrogen sulfide and any oxygen taken up will remain in the water. A very slight increase in salinity will increase the oxygen corrosion rate considerably. A minor inflow of seawater into a geothermal system could make the water unsuitable for direct use.

The main types of scales encountered during utilization of Icelandic low-temperature geothermal fields are summarized in Table 1 (Kristmannsdóttir, 1989).

TABLE 1: Main types of scales encountered in Icelandic geothermal installations for low-temperature fluids

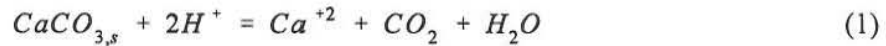
Types of scales	Location of scale	
	Inside well	In surface construction
Calcium carbonate (Calcite aragonite)	x	x
Magnesium silicate		x
Zinc silicate		x
FeS	x	x
Fe ₂ O ₃		x

Geothermal reservoir water is generally calcite-saturated at reservoir conditions, but will often become supersaturated by production (Arnórsson, 1989). There are three known naturally occurring polymorphs of calcium carbonate minerals, calcite, aragonite and vaterite. Studies of downhole deposits have revealed that they begin to form at the level of first boiling where they tend to be most intense. The volume of deposits diminishes upwards. For some fields no scaling tendency is observed from the water discharged at the surface. In others it can be quite intensive.

When the hot water is deaerated of acidic gases, the pH is elevated, which may lead to subsequent supersaturation and precipitation of carbonate in water of high ionic strength. Mixing will, in many instances, lead to instant supersaturation. Deposition may be accelerated by salinity or other catalysing effects such as rough surfaces or suspended materials.

Many experimental studies have been carried out to determine the solubilities of the calcium carbonate minerals in aqueous solutions. Boiling causes a drastic decrease in CO_2 partial pressures which leads to supersaturation and calcite precipitation. The supersaturation reaches maximum soon after boiling is initiated. At this maximum the water is almost quantitatively degassed.

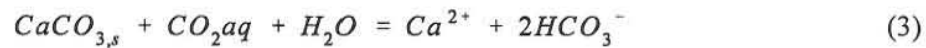
The solubility of calcite (and other calcium carbonate minerals) may be expressed by the following reaction:



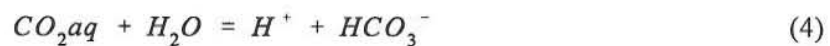
with the equilibrium constant being

$$\frac{(Ca^{2+})}{(H^+)^2} \times p_{CO_2} = K' \quad (2)$$

Parentheses indicate activity. The ratio of $(Ca^{2+})/(H^+)^2$ in geothermal water tends to vary with temperature, the reason being that it is controlled by some mineral buffer. It is evident that this buffer, together with calcite, will fix p_{CO_2} at any temperature and pressure. Dissolution or precipitation of the $CaCO_3$ phases calcite or aragonite can be written as the following chemical reaction:



Aqueous CO_2 will be in equilibrium with CO_2 vapour if a gas phase is present. A movement of CO_2 from the liquid to the gas phase will result in decreasing the concentration of aqueous CO_2 and will drive Reaction 3 to the left. CO_2 loss from solution, therefore, results in precipitation of $CaCO_3$. A parallel reaction is



Loss of aqueous CO_2 to the gas phase will drive Reaction 4 to the left and the pH of the solution will rise.

As can be seen from Reaction 3 a certain supply of CO_2 is required to maintain sufficiently high CO_2 partial pressure for calcite saturation (Reed, 1989). The solubility of calcium carbonate minerals in aqueous solution at any particular temperature increases with increasing partial pressure of CO_2 . The degassing of CO_2 leads to an increase in pH and a strong increase in carbonate ion concentration. It is mostly this latter increase that is responsible for making initially calcite-saturated geothermal water supersaturated through boiling. However, dissociation of calcium-bearing ion pairs, particularly $CaSO_4$, as water temperatures decreases may also contribute to the extent of supersaturation.

Siliceous scaling is not common by exploitation of low- to medium high-temperature water. The precipitation of silica normally does not occur until supersaturation with respect to opaline silica is reached and in low-temperature waters this does not happen at the temperatures prevailing in the hitaveitas (municipal heating services). The silica may precipitate and form stains in wash basins and

by leaky connections and faucets, but only in the hottest waters with the highest silica will there occur any scaling. Magnesium silicate scale has been found in two kinds of Iceland district heating systems, those which are based on heating fresh water, and those where there is mixing of geothermal and fresh water. The fluids precipitating magnesium silicates have a large compositional range (Sverrisdóttir et al., 1992). The Mg/Si ratios of the precipitates span two orders of magnitude, but peak around two main values.

Precipitation of other silicates is not common either. Mixing of fresh water into geothermal water may induce scaling by magnesium silicates. Magnesium concentrations in fresh water are generally much higher than in geothermal water. An exception is carbonate water where magnesium concentration can be quite high. Due to the inverse temperature dependence of magnesium silicate solubility, there is a great risk of their precipitation when fresh water is heated. The temperature and degree of deaeration, together with the pH, are the controlling factors for supersaturation. Precipitates from a mixture of geothermal and fresh water from the Reykjavík heating system show more complicated XRD-patterns (Sverrisdóttir et al., 1992) than those from heated cold water. Varieties of talc, saponite, sepiolite, and chrysotile are probably present.

The precipitation appears to be governed by the equilibrium and supersaturation of two well-defined magnesium silicate species, rather than by some kind of polymerization and subsequent annealing with time. The mineral formed in the unmixed heated freshwater is a serpentine mineral, probably a variety intermediate between chrysotile and antigorite. Minerals formed in mixed waters are richer in silica.

Special circumstances have given rise to scaling by hydrated zinc silicate, hemimorphite ($Zn_4(OH)_2Si_2O_7 \cdot H_2O$) and also willemite (Zn_2SiO_4). This kind of scaling has formed in brass knees in copper pipes and in galvanized steel pipes. Scales of metal sulfides and oxides may occur in combination with metal corrosion in pipes and other plant installations. As most metal sulfides are poorly soluble, such scale can be found in most metal pipes. Copper will be severely corroded in water containing hydrogen sulfide and subsequently copper sulfide will be precipitated. Iron sulfide, FeS_x will normally be deposited inside steel pipes carrying hydrogen sulfide water. In Iceland (Kristmannsdóttir, 1989) such scales are found to make a protective lining preventing further corrosion of the steel. Elsewhere like in the Paris basin (Criaud and Fouillac, 1989), a continuous corrosion of the steel and precipitation of iron sulfides have been found to take place.

In oxygen-containing water, a combination of corrosion and precipitation may create metaloxide scales. Outside corrosion of steel pipelines due to moisture in contact with the steel is the most serious problem. It will cause rapid inside corrosion if the concentration exceeds 15 ppb. Contamination of geothermal water with fresh water in the district heating systems produces corrosion. Oxygen diffuses through plastic pipes making the water corrosive to steel pipes.

To predict the potential danger of scaling and corrosion, computer programs like WATCH (Bjarnason, 1994) or SOLVEQ (Reed and Spycher, 1984) are used. The program WATCH is commonly used for interpreting the chemical composition of geothermal fluids. The program computes the chemical composition of downhole or aquifer fluids, and provides chemical analysis of water, gas and steam condensate samples collected at the surface. This includes the pH, aqueous speciation, partial pressure of gases, redox potentials and activity products for mineral dissolution reactions.

The WATCH program can also be used to compute the concentrations of resulting species, activity coefficients, activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in the study of scaling.

It is possible to predict the scaling potential if chemical data are known. One possibility is to calculate the ionic activity, Q , corresponding to different minerals in the brine and to compare it with the theoretical solubility, K , of the respective minerals. Usually logarithms of these values, $\log Q$ and $\log K$, are calculated using the WATCH program.

By using of the WATCH (or SOLVEQ) program, composition and speciation of the geothermal water in the reservoir can be calculated. Calculations can show if there is a general equilibrium in the water at the estimated reservoir temperature, if there has occurred mixing of different aquifers, or an inflow of cold water. Changes in the water by cooling, boiling or other processes within the system can be modelled and subsequent changes in chemistry evaluated. This is an important tool for the assessment of production characteristics of the water. Changes in geothermal water over time are also clearly seen by comparing the changes in mineral equilibrium in water samples from different times.

It is common practice (Reed and Spycher, 1984) to calculate and plot against temperature the $\log Q/K$ values, (saturation index), for various minerals likely to govern the chemistry of the water. When $Q < K$ the saturation index is negative and the solution under-saturated with respect to the mineral considered. When $Q > K$ the solution is supersaturated, and when $Q = K$ the solution is exactly saturated or in equilibrium with the mineral in respect. If the water is in equilibrium most of the curves will intersect the saturation line at almost the same temperature. If there occur two or more main intersections, the fluid is likely to have reequilibrated at a lower temperature, still keeping memory of an equilibrium at higher temperature.

The scaling potential is estimated by calculating $\log Q/K$. A positive value for the relative log solubility of a mineral means that the solution is supersaturated with respect to that particular mineral and theoretically it would start to precipitate. However, experience gained in different fields utilizing geothermal water shows that minerals normally do not start to precipitate as soon as the solution becomes supersaturated. Production data for low-temperature geothermal waters in Iceland show, for example, that calcite normally does not start to precipitate until $\log Q/K$ values reach 0.3-0.5.

3. MONITORING OF GEOTHERMAL SYSTEMS

During the exploitation of geothermal fields the energy extracted normally draws greatly on their natural power, and field response to exploitation may create problems during long-term utilization. When drawdown or pressure drop follows the pumping of water wells, there is a potential danger of inflow of cold ground water or seawater into the field (Kristmannsdóttir et al., 1995). This can produce cooling and changes of production characteristics. A change in the chemical composition of the geothermal water will often precede cooling of the field, and data obtained by chemical monitoring of the fluids may, therefore, give a warning in time for preventive action. As chemical changes will often precede changes in temperature and pressure, it is always recommended to monitor the chemical composition of the fluids in a geothermal system.

The infiltration of seawater into a fresh water geothermal system is relatively easily traced and will be detected early on by simple chemical monitoring. The inflow of cold fresh water into a geothermal system is often difficult to detect at an early stage and its detection requires a much more elaborate monitoring system than seawater infiltration.

Wells with inflow from two or more aquifers, each with its characteristic temperature and chemistry, are commonly exploited in Iceland and probably elsewhere also. Changes in the mixing ratio of water from different aquifers resulting from changes in pressure may affect production characteristics drastically.

In exploited low-temperature systems it is common practice to collect a sample for analysis of all main constituents (pH, volatiles, silica, Na, K, Mg, Ca, Al, Fe, Mn, Cl, Br, B, SO₄, F, NO₃, TDS) at least once a year from all fields and more frequently from fields where the water is slightly mineralized and there is fear of fresh water inflow (Kristmannsdóttir and Ármannsson, 1996). Occasionally samples for analysis of selected trace elements (Li, Sr, Cd, I, Zn, Hg, Pb, As) are collected. Where the geothermal water is highly mineralized or where seawater infiltration is expected, additional samples for chloride and sulfate analysis and possibly also selected cation, silica and even stable isotope analyses, are collected. The samples are often collected six times a year, but the frequency varies from one field to another and according to the state of development of the field.

The monitoring programmes applied may differ significantly for the various types of geothermal fields, and they have to be carefully outlined from the start and continuously adapted to new developments and experience during exploitation.

Monitoring, both of production and chemical properties, has proved to be an important tool in the management of geothermal production in low-temperature geothermal fields. The results have been used to forecast imminent cooling of geothermal fields or changes in their production characteristics. When scaling or corrosion is expected or is considered possible, test plates are installed into the well for monitoring. Even though theoretical studies and modelling of the system do not predict any corrosion and scaling, it is advisable to insert test plates into the system at critical points such as at wellhead, after mixing and deaeration in tanks and out in the distribution system. If modelling shows that there might be any potential danger of scaling or corrosion, such monitoring is absolutely required.

In order to expose corrosion/scaling coupons to the geothermal water for testing, a special device has been designed (see Appendix I) that allows the coupons to be entered and withdrawn without interrupting the flow (Thorhallsson, pers. com.). This is important in commercial installations where an uninterrupted supply of water is required. The coupons are held by two nylon screws to a long stainless steel stem. It is important to isolate the coupons from the stem using nylon washers to prevent galvanic corrosion. A gland, similar to that on a gate valve, seals against leaks by the stem. The pressure chamber is made from solid stainless steel, drilled out to accommodate the coupons, with 1 1/4" pipe threads to attach to a valve. The procedure to expose the coupons to the water is then simply to:

1. Attach the coupons to the stem with nylon screws and use washers between coupons and stem;
2. Withdraw the coupons into the pressure chamber;
3. Attach the pressure chamber to the valve;
4. After opening the valve the stem is pushed in, exposing the coupons to the flow; this requires moderate pressure to overcome the pipeline pressure;
5. After the coupons are in place inside the pipe the gland nut is tightened and handle secured so that the sample will stay in place during the testing period.

When the sample is withdrawn from the pipeline for inspection or removal, the reverse procedure is applied. First pull out the stem, close the valve and unscrew the pressure chamber. Remove the coupons for evaluation. The coupons are cleaned with acetone and weighed both before insertion and after inspection to evaluate weight loss or gain.

The evaluation consists in removing solids from the tube and analysing them first by microscope and then by XRD and XRF methods. For more accuracy the solids are analysed with a scanning electron microscope.

4. ROMANIAN GEOTHERMAL FIELDS

4.1 Distribution and general description of the fields

Geothermal exploration started in Romania in 1962 and 195 wells were drilled through 1994. These were put into production as they were completed and according to the possibilities of use. The distribution of geothermal activity in Romania is shown in Figure 1.

According to the characteristics of the geothermal reservoirs and to the territorial position, six distinct geothermal systems were identified, distributed within the main geological provinces of Romania as follows:

- Four are in the western part, near the border with Hungary and Yugoslavia, in the Pannonian Basin.
- One is in the Olt Valley, in the median part of Southern Carpathians.
- One is in the Moesian Platform area, north of Bucharest.

The main geothermal systems discovered on the Romanian territory are found in porous, permeable formations, such as sandstones and Pannonian siltstones, interbedded with clays and shales which are specific for the Western Plain (Cohut, 1993). Senonian gritstones, are however, specific for the Olt Valley or in carbonate formations of Triassic age in the basement of the Pannonian Basin and of Malm-Aptian age in the Moesian Platform.

The geothermal system which is situated in the western part of the country - called the Pannonian Depression, is the "hottest" zone in Romania. It is dissected into horsts and grabens. The Pannonian geothermal aquifer is multi-layered, confined and is located in the sandstones at the basement of the Upper Pannonian in an approximate area of 2500 km² along the western border of Romania from Satu Mare in the north to Timisoara and Jimbolia in the south. The aquifer is situated at depths of 800-2100 m. The thermal gradient is 45-55°C/km. The water temperature at the surface varies between 50 and 85°C. The mineralisation of the geothermal waters is 4-5 g/l. The type of water is sodium-bicarbonate-chloride.

The Oradea geothermal reservoir is located in the Triassic limestones and dolomites at depths of 2200-3200 m in an area of about 75 km² and is exploited by 12 wells with a flowrate of 140 l/s geothermal water with temperatures at the wellhead between 70 and 105°C. Mineralisation is about 0.9-1.2 g/l and there are small quantities of dissolved non-condensable gases such as CH₄, CO₂, He. The type of water is calcium-sulphate-bicarbonate. Both of the aquifers, the Triassic aquifer Oradea and the Cretacic aquifer Felix Spa are connected hydrodynamically and are parts of the active natural circuit of water.

The Borş geothermal reservoir is situated at about 6 km northwest of Oradea. The geological framework is completely different from the Oradea geothermal reservoir. This is a closed aquifer with a small

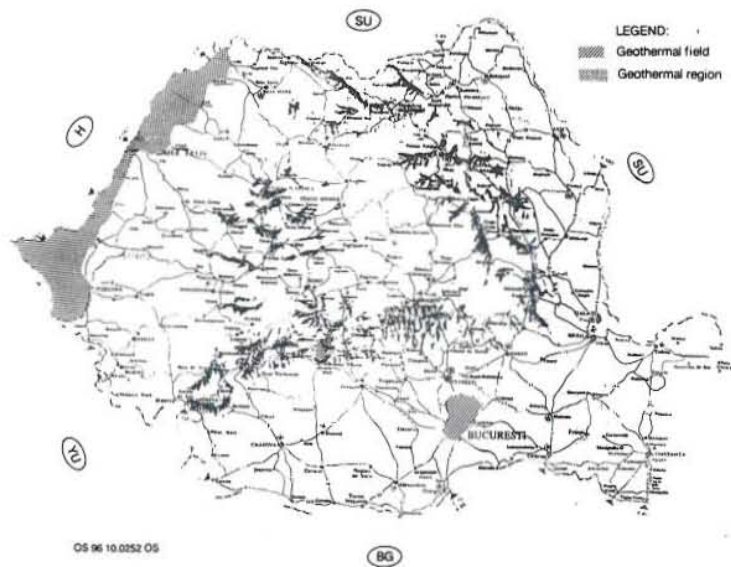


FIGURE 1: Geothermal fields in Romania

surface area of 12 km². The reservoir temperature is higher than 130°C at the average depth of 2500 m and the wellhead temperature is 115-118°C. The mineralisation is 13-14 g/l.

The Ciumeghiu geothermal reservoir is also located in the western plain of Romania, south of Oradea. The aquifer consists of gritstones at the average depth of 2200 m. Geothermal water is produced by artesian flow with a wellhead temperature of 105°C. The mineralisation is about 5-6 g/l.

In the southern part of Romania two geothermal systems were investigated and exploited which represent 18% of the exploitable geothermal resources of the country. The Getic Basin located in Olt Valley has a sunken and highly tectonically disturbed crystalline basement covered by alluvial Cretaceous deposits that are crossed by faults along which thermomineral water flows. Within the area investigated by drillholes, situated in the Cozia-Căciulata-Călimăneşti-Olăneşti regions, an important detritic fractured reservoir was identified with artesian water and intense thermal activity. This geothermal reservoir produces geothermal water with an artesian flowrate of 20-25 l/s and wellhead pressure of 16-20 bar from the siltstones of Senonian age at a depth of 1800-2200 m. The wellhead temperature is 90-95°C and the mineralisation is 14 g/l. The Moesian Platform, a geological province situated in the southern part of Romania, displays a complex structure, as a result of the dissection of the deposits in tectonic blocks and of their subsidence along deep N-S striking fractures. The geologic formations included in the region basement cover an almost complete stratigraphic sequence, beginning with Pre-Cambrian within the basement and ending with Quaternary deposits at the surface. The formation of interest for geothermal water consists of fissured, fractured and karstified carbonate deposits of Late Jurassic - Early Cretaceous age, that form a geothermal system 800-1000 m thick.

The Otopeni geothermal reservoir is located north of Bucharest. The aquifer belongs to the Moesian Platform and is situated at a depth of 1900-2600 m. Twelve wells were drilled in this area. The geothermal water has a wellhead temperature between 58-72°C and a mineralisation of 1.5-2.2 g/l. It contains about 25 ppm of H₂S. The total flowrate is 25-30 l/s.

4.2 Utilisation of geothermal energy in Romania

In Romania geothermal energy is used in various domains, leading to a saving in costs of classical fuel used for conventional energy production equivalent to 130 MW (thermal). The main uses are space heating and warm water preparation for domestic use, greenhouse heating, wood drying, milk pasteurization, flax and hemp processing, and fish farming. The energy equivalent gained from the geothermal resources is over 35,000 t.o.e./year distributed as follows: 47% space heating, 26% agricultural use, 15% industrial uses, 12% miscellaneous uses. About thirty wells are used for balneotherapy. The geothermal energy provides heating for more than 3000 conventional dwellings, several administrative buildings and commercial spaces, and about 47 hectares of greenhouses (Cohut, 1993).

Some geothermal water accumulations have a high content of combustible gas. When the proportion of methane is 80-90%, this provides a combustible gas fraction of 1-2 Nm³/m³ of water with a heating power of 8500 kcal/m³. For more efficient and complete use of the geothermal energy available in such water, a company has started to use this gas.

In the west part of the country, geothermal water is used as industrial water for hemp and ceramic factories. It is also utilized for domestic use and for heating swimming pools. In the southern part of Romania, geothermal water is used for heating houses and to provide domestic tapwater. In some resorts, geothermal water is used for heating hotels and recreation houses as well as for balneology.

Geothermal water is used in open pools and indoor swimming pools. In some areas the geothermal water is well fit for balneological use and for recreation facilities. There are also sixteen thermal spas in operation using geothermal water, which treat over 600,000 people per year. An example of such a resort is in the north Bucharest area, the Bucharest Institute of Balneo-Physical Therapy, where the water produced is a sodium-chloride, low concentration iodide water. It is used in external cures for balneo-therapeutic such as rheumatics and post-traumatics applications and peripheral nervous system applications.

Considering the outstanding special therapeutic properties of the geothermal water in the north of Bucharest, where the microclimate is ideal for recreation and the landscape of the area pleasant, it is expected that the Snagov resort (near Bucharest) will become an attraction for investments in tourism, recreation and health.

Another thermomineral water deposit which is used for therapy is situated in northwest Romania. In this region the geothermal gradient is higher than in other zones with similar structure, permitting the infiltrated water to emerge at the surface as thermal water. There are two resorts which contain abundant treatment facilities indoor and outdoor, sanatoriums and hotels. The waters of these resorts were known even during the Roman period. The 1 Mai resort is situated 8 km from Oradea, at 140 m altitude. In this resort there are about 30 thermal springs with temperatures in the range 28-42°C and their waters gather into a lake. The resort settlements take their water from the artesian spring "Izbuc" which resulted from drilling in 1885. There is also a sapropelic mud used for treating different diseases, and due to the high temperature in the lake, a flower very rare in Europe, *Nymphaea Lotus Thermalis*, a definite tourist attraction.

In order to succeed with the projects, Romania needs support, both in research and to obtain modern equipment and technology for efficient use of the geothermal energy, to build tourist and balneological facilities that would benefit by use of this energy source.

5. THE ORADEA GEOTHERMAL FIELD

5.1 Description of the field

One of the main geothermal reservoirs exploited in Romania is located in the western part of the country. The Oradea reservoir is an integrated part of this principal reservoir. The production history shows that it is an open reservoir. Its natural recharge is from the Apuseni Mountains, located about 80 km to the east of Oradea city. Borş is situated near Oradea. Both Oradea and Borş reservoirs are located in fractured Triassic limestones and dolomites (Roşca, 1993).

Oradea city is situated in the western part of Romania in the Pannonian Basin geothermal system. The reservoirs identified in the area are very different from others located in the Pannonian Basin. Three geothermal reservoirs have been identified within Oradea city and the surrounding area, known as the Oradea geothermal field. The reservoirs are usually named after towns or villages located in or close to the respective geothermal fields. The main reservoir is situated almost entirely within the Oradea city limits. It is hydrodynamically connected with a second reservoir in the Felix Spa resort, about 10 km southeast of Oradea. The Felix resort is 9 km southwest of Oradea and 3 km from 1 Mai resort. It is also situated at 140 m altitude. It is in a valley, surrounded by hills covered with forests. The "Balint" spring drilled in 1885 is the greatest among all the thermal springs in Romania, with a flow of 17,000 m³/day. The thermomineral water deposit, Oradea-Felix-1 Mai, is unique from a hydrodynamical and geological point of view. The third reservoir is near the Borş, 6 km northwest of Oradea.

By ^{14}C dating the water was found to be about 20,000 years old. The recharge area is in Pădurea Craiului mountains and the Borod Basin. Although there is a significant recharge of the geothermal system, the exploitation with a total flowrate of 300 l/s generates a high pressure drawdown of the system which is prevented in part by reinjection as a result of the successful completion and operation of the first doublet in the Nufarul district in Oradea town.

Geothermal energy utilization in Oradea consists of space heating and hot tap water, greenhouse heating, indoor and outdoor swimming pools, heating of indoor swimming pools, industrial space heating (two factories), milk pasteurisation (80,000 l/day), industrial hot water, intensive fish farming, pilot binary power plant (500 kW), grain drying, and wood drying (8,000 m³/year). At the Felix Spa resort the geothermal water is used for recreational and health bathing and its therapeutic properties have been known for a long time.

The Borş reservoir is a confined aquifer. The reservoir temperature and pressure distribution indicate a hot water upflow between Oradea and Borş. The temperature in the Oradea reservoir decreases from northwest to southeast in the Oradea aquifer and continues to decrease into the Felix reservoir. In the Felix Spa resort there are natural hot springs with temperatures between 35 and 50°C. The chemical composition of the geothermal fluid in the Felix reservoir is the same as in Oradea. The chemical composition of geothermal water from Borş reservoir is different from that of the Oradea reservoir.

5.2 Production history

Of the boreholes that have been drilled into the Oradea reservoir, eleven are used as production wells and one for reinjection. Data for the production wells are presented in Table 2.

TABLE 2: Oradea geothermal reservoir

Well no.	Drilling year	Wellhead pressure (bar)	Depth (m)	Wellhead temperature (°C)	Artesian flowrate (l/s)
4004	1963	0.6	2170	79	8
4005	1963	0.4	2050	90	7
4006	1964	0.3	2000	80	6
1709			2800	96	6
4767	1975	2.1	2270	105	20
4796	1981	1.2	2000	84	16
4797	1981	0.5	2040	70	15
4795	1982	0.2	2670	91	3
1716	1982	0.4	2550	86	3
1717	1982	1.1	2230	98	5
1715	1983	0.6	2250	70	11

The total installed capacity is at present 35 MW_{th} corresponding to a flowrate of 150 l/s of geothermal water at a mean temperature of 85°C. All the production wells are currently discharged in artesian flow. The well design and the rock formations in the Oradea and Borş reservoirs are similar. The possibility of doubling the yield of the wells in the Oradea reservoir by pumping is considered a realistic estimation. Increasing the production rate to 300 l/s means that all the extracted water has to be reinjected, not only to provide a pollution free disposal method but also to sustain the reservoir pressure. Too great a

pressure decline both in the Oradea and Felix reservoirs will eventually cause the natural hot springs there to dry up.

In the Borş reservoir five wells have been drilled at present: two are reinjection wells and three are production wells (Roşca, 1993). The reinjection wells are used to sustain the reservoir pressure and artesian flow of the wells. During the summer, additional cold ground water is injected to compensate for exploitation losses. Within the production wells two are used to provide base load and the third for peak load for the heating of 6 hectares of greenhouses. The wellhead pressures are 12 and 14 bars, respectively, for the two base load producers, each yielding 15 l/s at an operating pressure of 7 bars. The maximum flowrate from all producers is 50 l/s in artesian flow under the same operating conditions. The geothermal fluid is partially degassed, passed through heat exchangers and then reinjected. The injection pressure does not exceed 6 bars.

In the beginning of exploitation scaling problems were encountered. Scaling is effectively prevented through a combination of thermodynamic and chemical inhibition. The pressure is maintained above the CO₂ saturation pressure to prevent a great increase in pH and the Romanian antiscaling product Ponilit is additionally injected into the well. The most economical way to do this is to keep the pressure at 7 bars while the chemical inhibitor is injected into the well at a depth of 450 m by a dosing pump at a rate of 5 g/m³. The separated gases are currently released into the atmosphere and the environmental pollution is insignificant.

It is also possible to heat more greenhouses in this area using the geothermal water available in artesian flow from the wells already drilled. If the temperature of the return water is kept as low as possible by temperature controlled valves and the total flow from the three production wells is used to provide base load, the greenhouse area using geothermal energy could be doubled. Cohut (1993) showed that production can be doubled without causing a significant temperature decrease in the reservoir for at least 15 years.

5.3 Production characteristics of geothermal fluids

In the Oradea geothermal field corrosion problems have not been reported up to the present. The Oradea geothermal water is neutral to slightly acidic, while the Borş geothermal water is slightly basic. The concentration of dissolved solids in geothermal water in Oradea is relatively low (about 1200 ppm). The solution is slightly supersaturated with respect to anhydrite, but no scaling problems have been encountered at high temperatures. When the temperature of the geothermal water decreases below 50°C, it becomes supersaturated with respect to chalcedony. No real scaling problems are expected, however, until the temperature decreases below about 20°C. The salinity of geothermal water from Borş is very high, 4000-6000 ppm. Scaling problems have been encountered there.

Selected data on chemical composition of geothermal waters in the Oradea geothermal area are presented in Tables 3-6. There is generally a lot of scatter in the data; there may be contamination in the first samples, silica may have precipitated in some samples, but many differences may just be due to poor analytical quality.

The data were selected from a large data base, but as the difference between the cation and anion charges exceeded 10%, only a few analyses could be considered. The results presented in this report are, therefore, not very accurate. Data with ionic balance within admissible limits were selected, but many chemical components were omitted and, hence, the ionic balance does not reflect exactly the reality. An attempt was made to span the entire production time and, if possible, to select one analysis from each year.

TABLE 3: Chemical composition of geothermal water from well no. 4796, Oradea geothermal area, in mg/l

	1981	1983	1986	1987	1988	1989
pH	6.5	6.8	6.6	6.4	6.9	7.2
CO ₂	149.5	134.5	143.1	151	138.7	132
SiO ₂	54		55	86	61	53
Na ⁺	30		30		22	42.5
K ⁺	14		14.5		3	8.1
Ca ²⁺	245.08	223.29	245.08	220.44	229.05	240.48
Mg ²⁺	42.21	57.31	42.21	72.96	56.18	36.48
SO ₄ ²⁻	626.8	567	639.8	662.1	639.8	654.3
Cl ⁻	24.8	17.7	29.4	19.5	23	19.6
TDS	1196	1177	1362	1178	1253	1118

TABLE 4: Chemical composition of geothermal water from well no. 4797, Oradea geothermal area, in mg/l

	1983	1984	1986	1987	1988	1989
pH	6.5	7.4	7.45	6.9	7.5	6.8
CO ₂	149.7	110	113.7	133.8	134.4	114.8
SiO ₂			57.5	71	54	41
Na ⁺	45		5	23	36	13
K ⁺	15		2	6	4	2.7
Ca ²⁺	191.58	212.82	253.1	227.12	213.83	244.49
Mg ²⁺	26.93	91.81	85.55	40.53	64.81	60.8
SO ₄ ²⁻	510.7	676.5	809	593.1	688.8	723.8
Cl ⁻	10.6	7.1	17.9	17.7	17.7	12.5
TDS	967	1195	1214	2652	1573	1118

TABLE 5: Chemical composition of geothermal water from well no. 4767, Oradea geothermal area, in mg/l

Year	1976	1977	1979	1980	1984	1986	1987	1988
pH	6.65	6.92	7.03	6.9	7.1	6.9	6.8	7
CO ₂	165.6	175.5	165.5	165	154	167	189.2	180.6
SiO ₂	90.9	83.3	76.8	89.4		74.5	104	114
Na ⁺	46	53.5	47.5	31		45.2	40	23
K ⁺	12	14.9	14.8	9		12.5	3	10
Ca ²⁺	179.56	176.35	166.73	180.36	127.86	166.73	110.22	260.32
Mg ²⁺	28.94	26.63	33.56	35.87	68.34	33.56	54.72	20.18
SO ₄ ²⁻	455.4	448.7	455.8	452.2	393.4	454.2	357.2	522.5
Cl ⁻	21.3	19.1	19.6	20.8	20.2	18.4	31.9	31.9
TDS		1010	960	1005	865	983	1701	813

TABLE 6: Chemical composition of geothermal water from Borş, in mg/l

Year	1976	1979	1981	1983	1984	1986	1987	1988	1989
pH	6.67	6.65	7.15	6.7	7.4	7.5	6.6	6.5	7
CO ₂	86	1426.9	1174.2	1169.3	1166	1042.3	1170.3	1179.1	871.2
SiO ₂	195.6	117.6	106	106			122	80	114
Na ⁺	4660	4671	4484.4	4950	4707.2	5198.9	4500	4000	3419.1
K ⁺	140	134.2		80	121.8		220	550	379.9
Ca ²⁺	159.31	94.58	75.15	19.24	39.16	55.11	84.76	133.6	116.23
Mg ²⁺	8.02	40.47	22.19	16.29	1.7	28.33	39.76	24.37	17.02
SO ₄ ²⁻	1992.6	179.6	139.5	144.8	131.3	137.4	135.4	170.4	170.4
Cl ⁻	6399.7	6282.8	6075.5	6737.4	6560.1	7269.3	6560.1	6205.5	5311.1
TDS		11860	11826	12367	12395	13337	11647	11201	9810

Carbonate scaling potential was estimated. The saturation index of calcite in the geothermal waters from both the Oradea and Borş reservoirs was calculated for the wellhead temperature. The scaling potential is estimated by calculating log Q/K as explained in Chapter 2. As we can see in Figure 2, in well 4796 Oradea, a potential scaling can be expected in the future as the log Q/K for calcite has been increasing since 1988. A value of log Q/K for calcite exceeding 0.5 is by experience considered to be very dangerous. The calculation was made at 84°C, the wellhead temperature.

For Oradea well 4797, the WATCH program calculated the log solubility of calcite at 70°C, which is the wellhead temperature. Figure 3 shows the points are scattered and for several years we might have expected to get scaling problems but no scaling problems have been encountered, maybe thanks to the low chloride concentration. In the later years, the supersaturation of calcite decreased. In 1983 the solution was undersaturated, after 1984 it became supersaturated and after 1988 again undersaturated. This behaviour could indicate mixing of water from different aquifers with different temperatures if the analyses are indeed correct. One would suspect inaccurate measurements of Ca and carbonate as the values scatter considerably (Table 4).

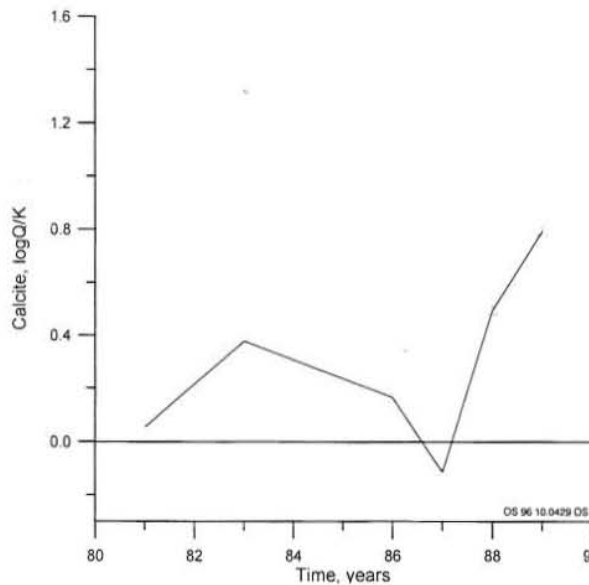


FIGURE 2: The saturation index for calcite for Oradea well 4796 against time at the wellhead temperature 84°C

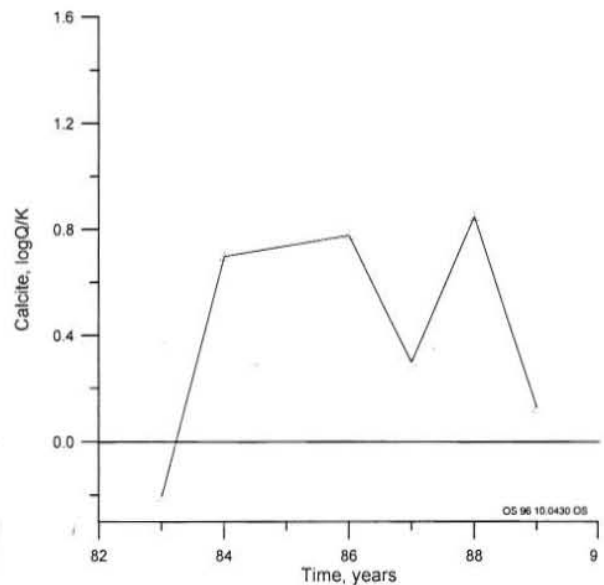


FIGURE 3: The saturation index for calcite for Oradea well 4797 against time at the wellhead temperature 70°C

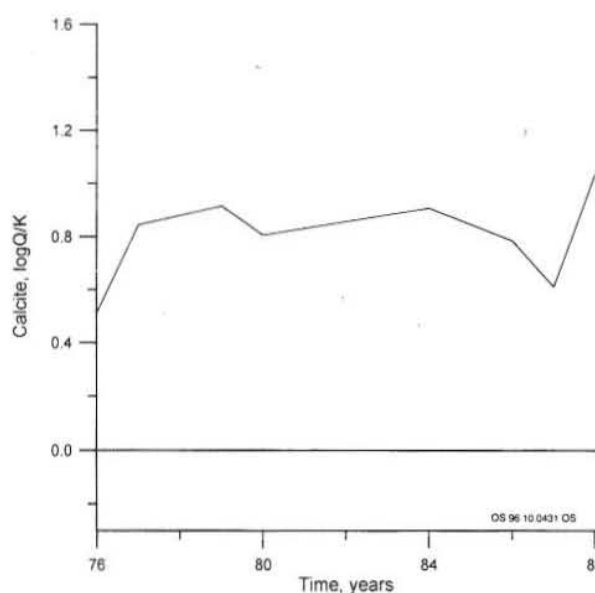


FIGURE 4: The saturation index for calcite for Oradea well 4767 against time at the wellhead temperature 105°C

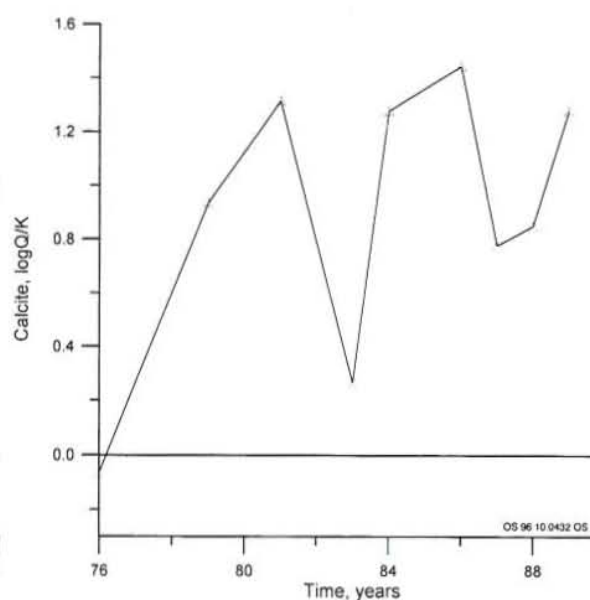


FIGURE 5: The saturation index for calcite for geothermal water from Borş against time at the wellhead temperature 115°C

The solubility of calcite was calculated for the Oradea well 4767, where the temperature of geothermal water is 105°C. As Figure 4 shows, the log Q/K values for calcite are within the range 0.5-0.9. After 1984 the calcite value decreased and since 1987 it started to increase again to very high values. The chloride concentration is very low, but if there is a small amount of oxygen, scaling problems and corrosion of the pipes might appear.

The geothermal water from Borş reservoir has a temperature of about 115°C. It is rather saline water, with the salinity about 5000 ppm Cl⁻ in 1976, and increasing to 7500 ppm Cl⁻ in 1988. Serious corrosion problems were encountered. Figure 5 shows the log Q/K values of calcite are very high and scaling problems are encountered.

In 1976 the value of calcite was below zero; the water was undersaturated, but the solution became more and more supersaturated with time. The supersaturation of calcite could be due to deaeration and boiling. This means that the CO₂ goes out from the water, and the equilibrium



will be driven to the left, favourable for calcite deposition. Also, the temperature of the geothermal water is rather high. If we assume the water boils, degassing of CO₂ will occur and deposition of calcite will follow.

Addition of acid to geothermal wells with calcite scaling problems has been used experimentally in some geothermal fields. But care should be taken, since well casing and other equipment can be corroded by the acidic solution when a sufficiently stable corrosion inhibitor is lacking (Thórhallsson, 1996).

To decrease the pH below a certain value where no calcite scaling can form may be technically possible, but not economically feasible. Excessively large amounts of acid are required to obtain even a fairly small decrease of pH as many geothermal fluids have an extremely large flowrate and buffer capacity.

The utilization of scale inhibitors is a practical method for fighting scaling problems. Inorganic phosphates can prevent precipitation of almost insoluble compounds if added to the super-saturated CaCO_3 solution in small quantities (Ármannsson, 1996). The proposed mechanism suggests that the phosphate keeps large quantities of CaCO_3 in solution while it begins to crystallize. Practically, the phosphates do not prevent the initial nucleation, but maintain microscopic size and prevent growth of the crystalline nuclei.

5.4 Monitoring of scaling and corrosion

A geothermal reservoir has to be monitored on a regular basis. A model is then used to forecast the behaviour of the reservoir for different production scenarios. Chemical analysis of the extracted water should be carried out at least once a year or, even better, every spring just before production is stopped and every fall just after production is started. It is also recommended that the concentration of certain components should be measured weekly. For the geothermal water from the Oradea reservoir, the concentrations of Ca, Mg and SiO_2 are significant and should be checked weekly. For the Borş reservoir besides SiO_2 it is more important to check, Na and Cl weekly, since they control the salinity of the geothermal water. Changes in the concentrations of these components could give advance warning of water inflow from different aquifers, especially cold water.

The amount of extracted and injected water is recommended to be monitored daily, four times a day if possible. The wellhead temperature and the wellhead pressure or water level should also be recorded. Data acquired by monitoring is used in reservoir modelling of the field which forecast changes within the reservoir at different production rates, such as pressure or temperature decrease. The management of the fields is based on such reservoir simulation studies.

6. THE SELTJARNARNES GEOTHERMAL FIELD

6.1 Description of the field

The Seltjarnarnes geothermal field is located within the town Seltjarnarnes, which is one of the suburbs of Reykjavík, the capital city of Iceland. The Seltjarnarnes field is located within the Kjalarnes caldera. Reservoir temperatures range from 80°C to over 140°C at 2700 m depth. The main reservoir rocks are Quaternary and become younger towards the southeast. The subsurface rocks can be divided into eight groups of basaltic lavas and hyaloclastites interbedded with a few small sedimentary beds and igneous intrusions, the latter increasing in frequency with increasing depth (Tulinus et al., 1987).

The Seltjarnarnes geothermal system consists of 3-4 different reservoirs with different temperatures and salinity. Drilling in the region started in 1965 (Kristmannsdóttir, 1986). A total of twelve wells have been drilled by now. All of the wells have at least three feed zones. Mixing of water from the different feed zones within a well causes calcium carbonate supersaturation of the water. This supersaturation is highest when the colder water from shallow feed zones mixes with hotter water from the deeper ones (Kristmannsdóttir and Ármannsson, 1996). The scaling potential increases with increasing temperature difference between feed zones.

The deepest reservoir yields 140°C water and extends from about 1500 to at least 2700 m. No temperature change has been observed at the lower levels of the field during the last fifteen years. The highest measured temperature ($>140^\circ\text{C}$) is in well SN-6 at 2700 m depth. The average wellhead temperature is 110°C .

TABLE 7: Wells drilled in the Seltjarnarnes field

Well no.	Year drilled	Depth (m)	Type
SN-1	1967	1282	Monitoring well
SN-2	1965	856	Monitoring well
SN-3	1970	1715	Monitoring well
SN-4	1972	2025	Production well
SN-5	1981	2207	Production well
SN-6	1985	2701	Production well
SN-7	1994	154	Exploration well
SN-8	1994	153	Exploration well
SN-9	1994	132	Exploration well
SN-10	1994	132	Exploration well
SN-11	1994	145	Exploration well
SN-12	1994	2714	Production well

6.2 Production history

Drilling in the Seltjarnarnes area started in 1965 and at the end of 1995 twelve wells had been drilled (Table 7), four production wells, three which now serve as monitoring wells and five shallow thermal gradient wells. The field has been exploited to provide hot fluids for the hitaveita of Seltjarnarnes. Before 1991 the average production was around 45 l/s. Since 1991 the average yearly production has been around 30 l/s because the tariff system for space heating was changed from a maximum flowrate system to one based on the energy consumed (a metering system). The salinity of the produced fluid has slowly increased due to the sea water infiltration, from about 1000 ppm of total dissolved solids to 3000-4000 ppm. Due to the high salinity the hot water is mostly used indirectly, through heat exchangers.

In 1972 the geothermal water was barely acceptable as drinking water and corrosion problems were feared because of the high salinity. The initial salinity was considered to be due to leaching of salt from sediments and hyaloclastites in the reservoir rocks. The stable isotope ratios $\delta^{18}\text{O}$ and δD are about -10.4 ‰ and -74.5 ‰, respectively, and indicate an origin in the inland mountains 90-100 km to the northeast of the Seltjarnarnes geothermal field. The $\delta^{18}\text{O}$ ratio has not changed significantly with time. The near constant value of $\delta^{18}\text{O}$ suggests recharge of meteoric water, whereas the increase in the chloride and sodium suggests an influx of sea water.

Several downhole samples collected early in the production period indicate that the initial concentrations of the total dissolved solids, chloride and sodium, were fairly uniform throughout the wellfield. In the first shallow drillholes the chloride concentration in the 70-80°C hot geothermal water was 400-500 mg/l, increasing with depth to about 700 mg/l. In the production wells the average chloride concentration in the produced fluid was about 500 mg/l at the beginning and increased upto 1400 ppm in 1986. Likewise the concentration of sodium has increased from approximately 300 ppm in 1966 to 800 ppm in 1986. The pH was about 8.4 at 20°C. The geothermal water has a low, but detectable concentration of hydrogen sulphide. It is close to equilibrium with respect to chalcedony and saturated with respect to calcite. The sulphate to chloride and calcium to chloride ratios at the reservoir temperatures are considerably higher than in seawater, whereas the sodium to chloride and potassium to chloride ratios are lower than for sea water. This is in agreement with water-rock interactions.

Well SN-12 was drilled in 1994. Prior to the drilling of well SN-12, five shallow exploration wells were drilled in the area to aid in the location of the new production well. The well was cased down to 800 m depth to prevent mixing with shallow cold aquifers. Only minor circulation losses occurred during the drilling of the production part of well SN-12. This was partly believed to be because the well was drilled with a minimum weight on the drill bit, resulting in very fine drill cuttings clogging the feed zones intersected. A one hour air-lift test, carried out at the completion of drilling of the well yielded less than 1.5 l/s with a 150 m water level drawdown. In addition, water could only be injected into the well at a very low rate at the end of drilling. Well SN-12 appeared, thus, to be almost non-productive at the completion of drilling. It was, therefore, decided to attempt to stimulate the well. During drilling of the other production wells in the Seltjarnarnes field minor, circulation losses were detected. They were better producers than well SN-12 appeared to be and were improved significantly by stimulation programmes at the end of drilling.

A comprehensive stimulation programme turned well SN-12 into a good production well (Tulinius et al., 1996). The productivity of the well increased by a factor of almost 60 by stimulation. The main feed zone of the well is at a depth of 2040 m with a temperature of 125-130°C. A smaller feed zone at 1070 m has a temperature of 85-95°C. Well SN-12 has been pumped continuously since November 1995. The production has been 26 l/s on the average, with a drawdown of about 50 m. The water temperature has been rising slowly to about 110°C at present. This is somewhat lower than anticipated prior to drilling, but the temperature is still rising.

During the last five years the changes in the water chemistry have accelerated. Most prominent is an increase in salinity. Serious corrosion problems have arisen in the heating system and they have increased along with the salinity of the water. The main reason for the increase in salinity of the geothermal water is believed to be the inflow of cold seawater at shallow levels. Cooling of the geothermal water is anticipated. There is also concern that scaling problems might appear.

6.3 Analytical results

Waters from two of the production wells in Seltjarnarnes were sampled for analysis using standard methods in the chemical laboratory at Orkustofnun. The credibility and usefulness of geochemical data depend on the methods used and the care taken in the collection of samples. If the sampling conditions are not well known, the significance of analytical results may not be fully appreciated. The sampling methods and preservation of samples may vary according to the nature of the geothermal water. If nothing is known about the water, one may have to take a somewhat more complicated sample, like several dilutions for silica measurements and precipitate H₂S for SO₄ analysis. After some information of the water composition is obtained, the sampling methods are adapted to those particular conditions (Trujillo et al., 1987). Sampling methods and analytical procedures are described briefly in Table 8 and in detail in Appendix II.

The results of the laboratory analyses are summarized in Table 9 and, for comparison, data from 1995 are presented in Table 10 (Kristmannsdóttir et al., 1995). As seen from the tables there are great differences between the calcium concentration in geothermal water in well SN-4 in 1996 in comparison to 1995. The calcium concentration does not fit very well with the measured chloride concentration and there is generally a lack of cations relative to anions. To try to find an explanation for all this, aliquotes of the sample (Rd, Fa, Fu) were analysed for Ca and Cl and it was found that the composition of the water had oscillated during sampling and the Fa sample had much lower chloride and calcium concentration than the Fu sample. This strange analytical result that was obtained in 1996 is due to the instability of well SN-4 during the period when the samples were taken. The production from well SN-4 was started just one day before the sample was taken and it is assumed that there were some perturbances in the well. Also, well SN-12 had been in exploitation for several months which may have affected the productivity of the lowest aquifer in well SN-4.

TABLE 8: Analytical methods used for the constituents determined

Constituent	Fraction	Method	Brief description	Standard	RSD%	D.I. (µg/l)
pH	Ru	Electrometric	A glass electrode in combination with a reference potential is inserted into the sample and pH and temperature values recorded.	Merk Titrisol pH 4,7,10	±0.1 pH unit	
CO ₂	Ru	Electrometric, titration	Sample pH adjusted to 8.2 with HCl/Na OH then titrated to pH 3.8 with 0.1N HCl using a pH meter.	Merk Titrisol 0.1N HCl	3.6 for 5-1500 ppm	1000
H ₂ S	Ru	Titration	NaOH added to make sample basic. Titrated with 0.001M HgAc, dithizone as indicator.		3.9 for 0.03-800 ppm	20
O ₂	Ru	Colorimetric	Measurements with Chem-metrics ampules			1
SiO ₂	Rd	Spectrophotometry	Iodine and thiosulphate added to destroy H ₂ S, ammonium heptamolybdate and HCl added. Absorption determined at 410 nm.	Natural thermal water from Spăstadir, the SiO ₂ concentration (~104 ppm) is determined gravimetrically.	1.8-2.5 for 0.87-67.3 mg/l	500
F	Fu	Selective electrode	TISAB buffer added, electrode inserted and potential read.	Merk 1000mg/l NaF/H ₂ O	3.5 for 0.85 ppm	2
Cl	Fu	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. Cl determined using a conductivity detector.	Merk Titrisol HCl/H ₂ O	2.9 for 10 mg/l	25
SO ₄	Fu/Fp	IC	Anions from a small volume of samples are separated by means of a guard column, a separator column and a suppressor column. SO ₄ determined using a conductivity detector.	Merk Titrisol H ₂ SO ₄ /H ₂ O	1.5 for 98.5 mg/l	20
B	Fu	Spectrophotometry	Sample buffered with NH ₄ Ac/Na ₂ EDTA/HAc Azomethine-H/ascorbic acid reagent added. Absorption determined at 420 nm.	Merk Titrisol H ₃ BO ₃ /H ₂ O		5
Na	Fa	AAS DA	A small amount of Cs solution is added and the sample directly aspirated into an oxidizing air-acetylene flame. Absorption read at 589.6 nm.	Merk Titrisol NaCl/H ₂ O	1.2-1.5 for 8.2-52 mg/l	1
K	Fa	AAS DA	A small amount of Cs solution is added and the sample directly aspirated into an oxidizing air-acetylene flame. Absorption read at 766.5 nm.	Merk Titrisol KCl/H ₂ O	7.9-12.5 for 1.6- 6.3 mg/l	1
Mg	Fa	AAS DA	A small amount of La solution is added to water sample which is directly aspirated into an oxidizing air-acetylene flame. Absorption read at 285.2 nm	Merk Titrisol MgCl ₂ /HCl	2.4-4.8 for 21-82 mg/l	1
Ca	Fa	AAS DA	A small amount of La solution is added and the sample directly aspirated into an oxidizing air-acetylene flame. Absorption read at 422.7 nm.	Merk Titrisol CaCl ₂ /HCl	1.7-3.3 for 9-36 mg/l	10
Al	Fa	AAS GF	Dried 30 s 125°C, ashed 30 s 1500°C, atomized 3 s 2400°C. Purge gas Ar 309.3 nm.	Merk Al(NO ₃) ₃ , 0.5M HNO ₃		1
Fe	Fa	AAS GF	Dried 30 s 140°C, ashed 30 s 1200°C, atomized 3 s 2100°C. Purge gas Ar 248.3 nm.	Merk Fe(NO ₃) ₃ , 0.5M HNO ₃		0.1
TDS	Fu	Gravimetric	Sample evaporated and dried at 105°C		2.6-3.8 for 190-1680 ppm	2500

AAS - Atomic absorption spectroscopy
 GF - Graphite furnace
 Fa - Filtered, acidified
 Fu - Filtered, untreated
 Fp - Filtered precipitated

DA - Direct aspiration
 D.I. - Detection limit
 Ru - Raw, untreated
 RSD - Relative standard deviation
 Rd - Raw, diluted

Using the WATCH program the ionic balance for geothermal water from well SN-12 in 1996 was calculated (see Appendix III) and was found to be 1%, indicating good quality of the analysis. The saturation index for calcite was calculated at the measured temperature, 108.8°C. It is rather high, almost 0.5, indicating the possibility of scaling problems in the future. The saturation index for calcite decreases by conductive cooling.

TABLE 9: Chemical composition of geothermal water from Seltjarnarnes wells SN-4 and SN-12 in 1996, in mg/l

	Well SN-4	Well SN-12
pH	8.4	8.4
CO ₂	8.7	10.5
H ₂ S	0.05	0.11
SiO ₂	100.5	95.7
B	0.24	0.24
Na	550	628
K	10.2	12.2
O ₂	0	0
Mg	0.3	0.26
Ca	295	532
F	0.56	0.62
SO ₄	227	283
Cl	1528	1744
Al	-	0.016
Fe	0.010	0.004

TABLE 10: Chemical composition of geothermal water from Seltjarnarnes wells SN-4 and SN-12 in 1995, in mg/l

	Well SN-4	Well SN-12
pH	8.4	8.3
CO ₂	11.4	7.8
H ₂ S	0.08	0.11
SiO ₂	100.2	98.9
B	0.22	0.26
Na	630	723
K	11.8	14.8
O ₂	0	0
Mg	0.36	0.51
Ca	520	594
F	0.6	0.51
SO ₄	277	286
Cl	1654	1930
Al	0.018	0.007
Fe	0.004	0.037

6.4 Production characteristics of geothermal fluids

As mentioned before the Seltjarnarnes water is somewhat saline and has become increasingly more saline with production. This has changed the production character of the water considerably (Kristmannsdóttir, 1986). The changes are different in different production wells and the differences are partly explained by different effects of the drawdown on mixing rates of the aquifers in the wells. All the wells draw from several aquifers, but in the most recent wells the shallowest aquifers are cased off. The shallower aquifers are more affected by inflow of sea water than the deepest ones, but the water appears to be highly affected down to at least 1000 m depth. Deep water from below 1700 m is about half as saline as the production water (the mixture of all) and water from below 2100 m has 10-15% of that salinity.

Well SN-4, the oldest production well, has a shallow casing and has cooled considerably with time and the water has become increasingly more saline. To evaluate these changes, saturation indexes, log Q/K, for several minerals were calculated in samples from very early on until recently and plotted against time as described in Chapter 2. Figures 6, 7 and 8 shows three such diagrams for samples from 1972, 1984 and 1991.

An assessment of potential corrosion problems and an indication of conditions in the field can be obtained through careful interpretation of the analytical data (Arnórsson, 1991). Using the WATCH program the log solubility index for different minerals was calculated. A positive value for the relative log solubility of mineral means that the solution is supersaturated with respect to that particular mineral and theoretically it could start to precipitate.

Complete analyses from 1972, 1984 and 1991 from well SN-4 have been calculated in the WATCH program at production temperature and by cooling in steps of 20°C (Figures 6, 7 and 8). The data from WATCH program are presented in Appendix III.

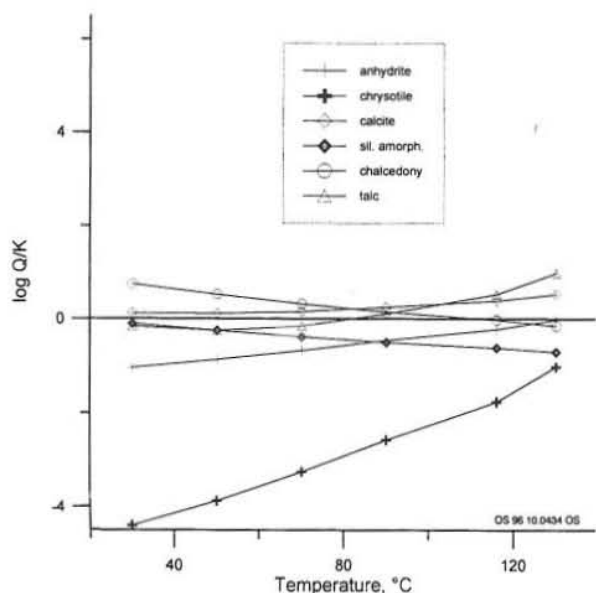


FIGURE 6: LogQ/K vs. temperature for selected water from well SN-4 Seltjarnarnes in 1972

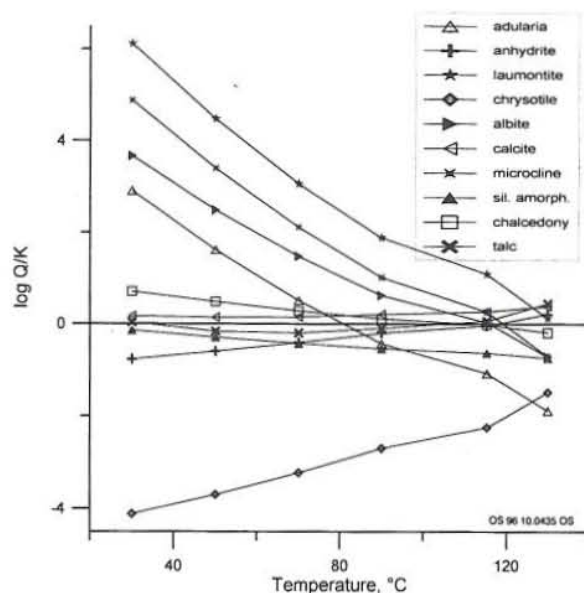


FIGURE 7: LogQ/K vs. temperature for selected water from well SN-4 Seltjarnarnes in 1984

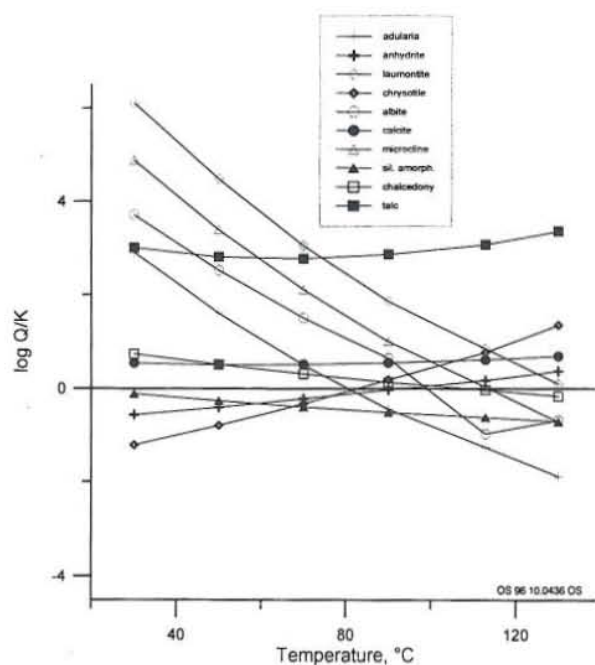


FIGURE 8: LogQ/K vs. temperature for selected water from well SN-4 Seltjarnarnes in 1991

amorphous silica are undersaturated as in the sample from 1972. Adularia crosses the equilibrium line at about 80°C. Calcite is slightly supersaturated. The equilibrium is slightly perturbed, probably due to the mixing of waters from aquifers at different temperatures. The curves for microcline, albite, chalcedony, calcite, anhydrite and talc intersect the saturation line at or near the measured temperature or lie close to the saturation line. At the measured temperature, 115.3°C, chrysotile, adularia and amorphous silica are obviously undersaturated. When the temperature of the geothermal water decreases the minerals laumontite, microcline, albite and adularia become supersaturated. At the well head temperature there are no scaling problems anticipated.

In the sample from 1972 (Figure 6) all elements were not measured, like aluminium and iron, which restricts the number of minerals for which log Q/K can be calculated. Most of the minerals calculated are found to be fairly close to saturation at chalcedony temperature. It is obvious that the chrysotile and the amorphous silica are undersaturated. Calcite is slightly supersaturated at about 120°C there is an equilibrium with anhydrite and chalcedony. Even if the temperature of the geothermal water were to increase with time, chrysotile and amorphous silica would still remain undersaturated. The equilibrium temperature for chalcedony corresponds to the measured temperature: 116°C. The water is close to saturation with calcite. If the temperature increases above 120°C we can expect scaling.

In the sample from 1984 (Figure 7) more elements were analysed and, therefore, more minerals could be calculated. Many minerals show equilibrium near the chalcedony temperature. Chrysotile and

In the sample from 1991 (Figure 8) the diagrams are much more scattered and intersect mostly between 80-110°C. This can be interpreted by an increased importance of the colder 80°C aquifers in the production water. At the measured temperature the minerals are undersaturated, saturated or near the saturation line. There are no scaling problems. Only talc is supersaturated, but this does not create problems. Minerals are in equilibrium at different temperatures in the interval 80-120°C.

Figure 9 shows the variation of calcite in time, from 1972 to 1995. After 1981 supersaturation of calcite increased to a dangerous value but has not continued to increase. Experimental data for low-temperature geothermal water in Iceland show that calcite may start to precipitate when log Q/K values range from 0.3-0.5. In well SN-4 from Seltjarnarnes there have been no scaling problems, although the log Q/K for calcite is rather high. Recently, the values for log Q/K of calcite have been in the range 0.4-0.5 and no scaling has been observed.

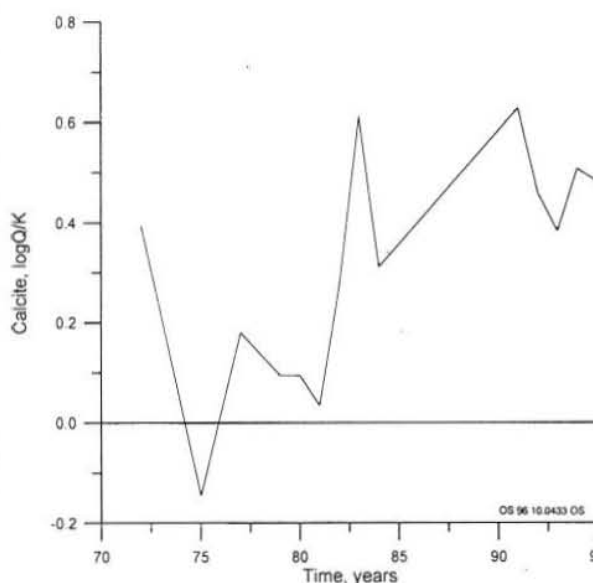


FIGURE 9: Changes in calcite with time in geothermal water from well SN-4, Seltjarnarnes

6.5 Monitoring of scaling and corrosion

The Seltjarnarnes geothermal system consists of three main reservoirs. All of them were found to be affected by seawater inflow. Temperature logging and deep water sampling of unproductive wells suggest that the seawater inflow occurs at shallow depth in the system. After 1984 new production wells were drilled. They were cased to a much greater depth than the older wells. Cooling has not been observed in either the production water or in the wells. Deep water temperature, calculated from geothermometers, has not changed significantly either, implying that no imminent changes in temperature are to be expected. The infiltration of seawater into the Seltjarnarnes geothermal field has, thus, strongly affected the chemical characteristics of the water, even though it has not caused any cooling so far (Kristmannsdóttir et al., 1995).

The Seltjarnarnes geothermal water was somewhat saline in 1972, but the chloride concentration of the water was then, below the valid limit for drinking water (600 mg/l). Almost no changes were observed in the chemistry of the water during the first 5-6 years (Figure 10). Then the salinity increased slowly for the next 4-5 years and sharply during the years 1983-1986. Since then there was at first a slow increase in salinity and then it stopped because of measures taken to reduce field production. In 1990 the consumption of hot water decreased. Since then the pressure of the system has been recovered, and in 1991 the increase in salinity appeared to have been halted or even reversed.

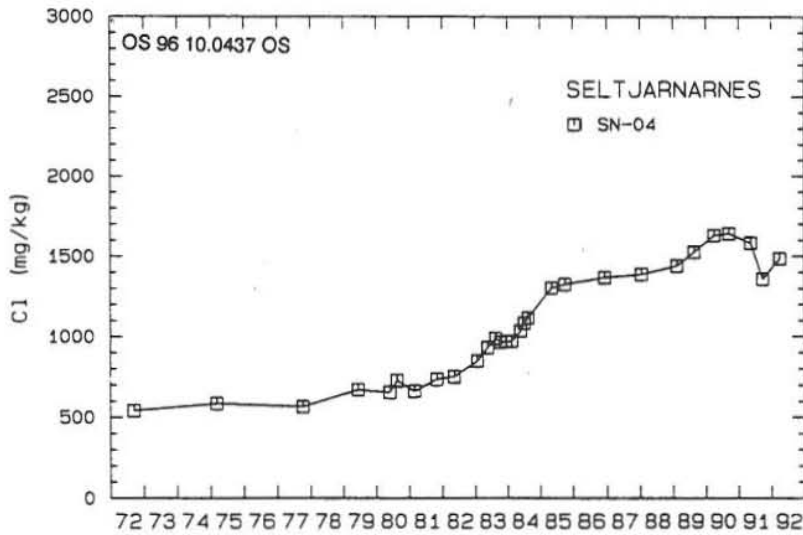


FIGURE 10: Changes in chloride concentration with time in water from the main production well in the Seltjarnarnes geothermal field

As the salinity of the production water increased, a greatly increased corrosion rate was observed, especially in steel radiators. Even though there is no dissolved oxygen in the geothermal water at the wellhead there always appears to be a minor diffusion of air into domestic circuits. At the salinity level reached by the Seltjarnarnes geothermal water, oxygen corrosion is rapid even at very low concentrations of dissolved oxygen (Thórhallsson, 1996).

Changes in the yield of different aquifers, and mixing within the wells, have caused substantial supersaturation of calcium carbonate in the water. Problems due to scaling may still be expected in the system and test plates have been installed for monitoring.

Monitoring by test plates has not been continuous in the heating system in Seltjarnarnes, mostly due to the trouble of stopping production for inserting and removing the plates. It has been planned for some time to install a scaling monitoring device of the type described in Chapter 2. The corrosion coupons were finally installed at the well head of SN-04 August 1996 and the plates were inspected twice, first on September 4th after two weeks and again on the September 18th. Unfortunately, there was very little time available for me to follow the test and production was insignificant from the well during those weeks, making the test less interesting than being hoped. The test plates showed insignificant changes when inspected after the first two weeks and later four weeks. Only a slight brownish gray discontinuous coating could be observed, much too little for any possible analysis.

The scaling monitoring device could not be installed at the well head of well SN-12 until late September, which excluded any monitoring of that well within the scope of this project. When the scaling monitoring device was installed in well SN-04 a thermowell, which had been within the pipeline for several years and had, thus, acted as a kind of corrosion/scaling monitoring device, was removed. This thermowell was consequently inspected and analysed.

The thermowell tube was analysed first by microscope. The tube was covered by deposition and was also somewhat corroded. It was of a brown colour, which appearance indicated that corrosion had started. A few crystals of white coloured deposited minerals were observed. Depositions of metallic colour were also seen. Microscopic identification was difficult, because the mineral was altered. The result of this inspection was that some scaling and corrosion were present on the tube.

After this preliminary inspection, the tube was analysed by X-ray diffraction, giving information about the existence of crystals in a solid sample. The sample was finely ground and the qualitative analyses made with XRD. The diagram obtained shows that there are magnetite crystals in the sample.

After this, the elements in the solid sample were analysed by X-ray fluorescence. A qualitative analysis was made to determine which elements were present in a specimen and also an analysis to gain a

semiquantitative appraisal of their concentration. The XRF diagram showed the presence of Si in a big amount and Fe. This means that there is silica deposition as well as corrosion of the pipe. Traces of Cr, Cu, Zn, Ti were encountered, but these may be due to contamination from the pipe. Also Ca was encountered, but in trace amounts, which means there is minor calcite deposition.

The thermowell was also analysed by the scanning electron microscope as shown in Figure 11. Black corrosion holes, filled up by solid depositions were seen. A cross-section was analysed and the results are shown in Figure 12. Fe is observed due to corrosion of the pipe and Si due to deposition. Traces are also seen of Ca, Mg, S and depositions of minerals with Ca and Mg. In the microscope a few yellow white crystals were observed, which are believed to be due to a deposition of iron sulphide, as S was identified in the scanning electron microscope. Traces of Cr are probably from the pipe material.

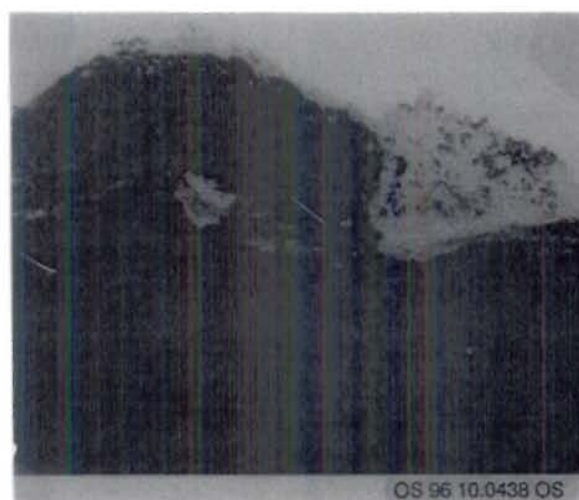


FIGURE 11: The surface of the tube of the thermowell

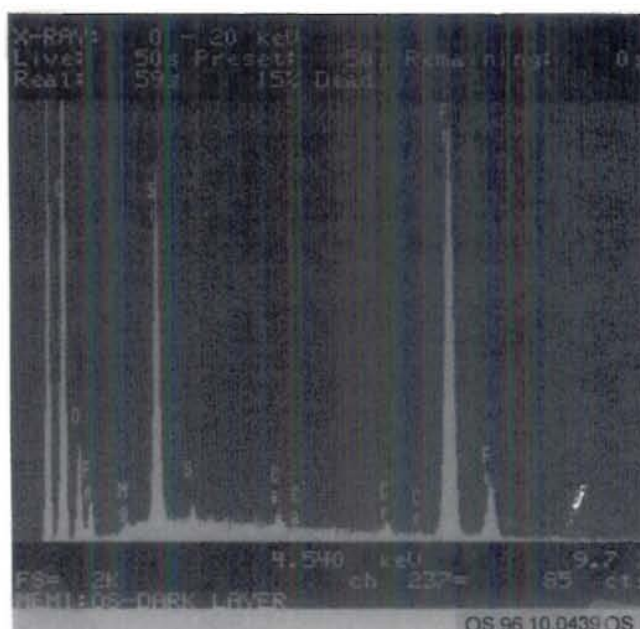


FIGURE 12: Electron microscope analysis of a sample from the surface of the thermowell

7. DISCUSSION AND CONCLUSIONS

The chemical composition of some geothermal waters from Romania and Iceland were interpreted by using the WATCH program, which gives information about the mineral equilibrium and a basis to assess possible scaling and corrosion problems. The Oradea geothermal field in Romania and the Seltjarnarnes geothermal field in Iceland were chosen for study.

Chemical analyses from several wells from Oradea and Borş (6 km from Oradea) were selected for interpretation. The chemical composition of the geothermal water in Oradea is different from Borş. The chemical analyses were not complete, so it was not possible to calculate a saturation index for many different minerals, but a calcite saturation index, which is very important, was calculated. By evaluation of the calculation of the saturation indexes for calcite over time, severe scaling problems are not

anticipated in Oradea. In Borş the saturation index values are very high and scaling problems would be expected and have indeed been encountered. The salinity in geothermal water in Borş is very high and corrosion problems have appeared.

To prevent calcite deposition in geothermal water from Borş it is necessary to use inhibitors or to try to decrease the pH, but this is a very expensive operation and could produce corrosion in the pipe.

Samples were taken from two wells in Seltjarnarnes and total analyses were made. The results were compared to results of former years by using the WATCH program, and the saturation index for different minerals calculated. The diagrams showed a significant change during the last ten years, which is interpreted to be caused by mixing of water from aquifers with different temperatures.

For monitoring of scaling and corrosion, a scaling device (corrosion coupons) was installed in well SN-4 at Seltjarnarnes and observed after a month. The time was too short for a results, but a thermowell which was inserted into well SN-4 several years ago was analysed by microscope, XRD, XRF and a scanning electron microscope and silica scaling, a trace of calcite scaling and corrosion were identified.

In Oradea geothermal field it is recommended that water samples are collected regularly. Changes in chemistry with time can give useful information on cooling and mixing of water. Changes in the chemical composition of water are often seen before changes in temperature are measured.

The data obtained in a detailed chemical study can be used as a basis for monitoring chemical changes. Chemical monitoring is recommended for Oradea geothermal field where utilization has started. It is better to counteract scaling and corrosion problems before they occur. For monitoring of the reservoir and possible scaling and corrosion it is recommended to take samples for complete analyses twice a year, and weekly samples for selected components, also to install a scaling device at wellheads.

The use of geothermal water is acknowledged to be very important due to its economically and nonpolluting characteristics. The possible environmental impact from its exploitation can be foreseen to a large extent, measures taken to minimize their effects prior to exploitation, and unforeseen impacts can be kept at bay using monitoring programs.

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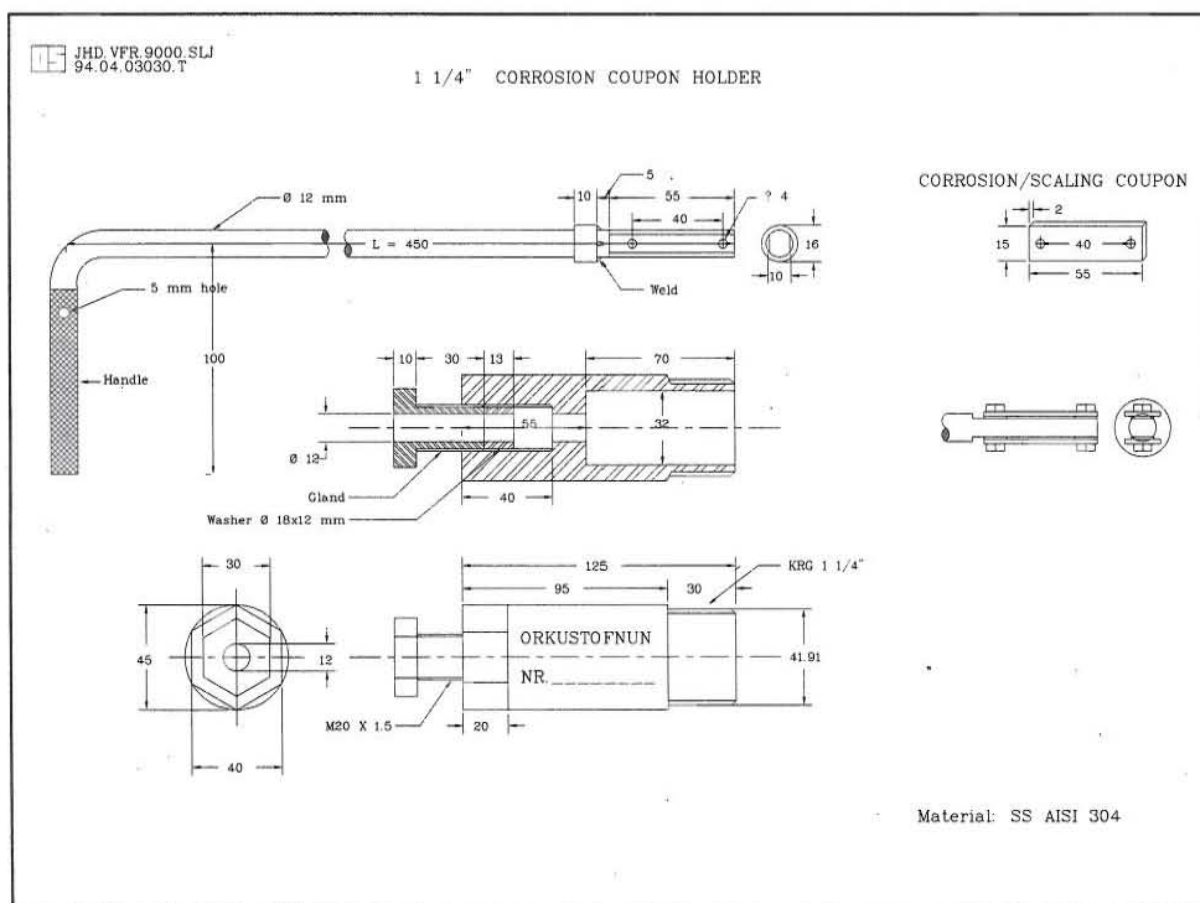
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APPENDIX I: A 1 1/4" corrosion coupon holder



APPENDIX II: Sampling methods and analytical procedures

Sampling from low-temperature wells

The following equipment is used:

- Plastic bottles, 500 ml, four per sample
- Plastic bottles, 100 ml, three to four per sample
- Air tight glass bulbs, one per sample
- Filter and filter paper (the size of the pores is 0.45µm)
- Finnpijets and clean tips
- One 100 ml and two 50 ml volumetric flasks for dilution (if SiO₂ expected >100 ppm)
- Equipment for measuring dissolved oxygen

- Cooling coil
- Rubber hoses and plastic connections
- Rubber gloves, water-resistant clothes and rubber boots
- Fittings
- Permanent marker
- Field record card and pencil
- Thermometer
- Map showing the location of the well
- Previous analysis of water if available
- Distilled water
- Solutions : HCl 6 N, HNO₃ suprapure, Zn(CH₃COO)₂ 0.2M if H₂S expected > 0.5 ppm.

For titration of H₂S (in situ) the following is also needed:

- Volumetric flasks, 50 ml, two
- Erlenmeyer flasks, 100 ml, two
- Gilmont Micrometer Buret
- Finnpiptet, preset at 5 ml
- NaOH, solution 5 N
- Acetone
- Dithizone powder as indicator
- Hg(CH₃COO)₂, solution 0.001N
- Tissues.

A general setup for the collection of hot water from a low-temperature production well is shown in Figure 1. The first time a sample is taken the name of the well and the number of sample is written on the card. When starting to connect to the well, one has to be very careful when opening for the water flow. The following describes the procedures:

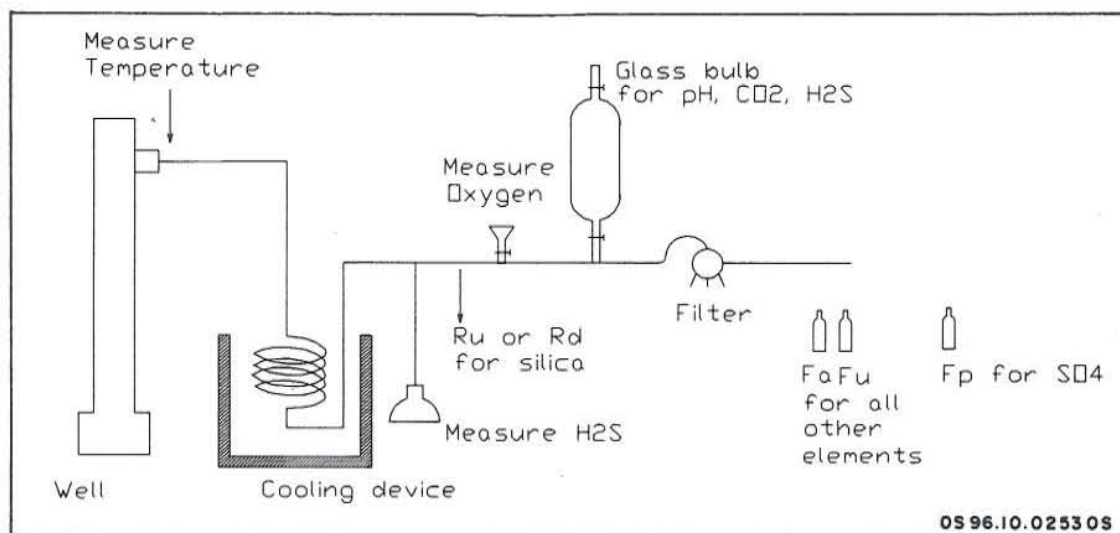


FIGURE 1: A general setup for collection of hot water from a low-temperature production well

- Cooling coil is submersed in cold water in a bucket; the temperature of cooling water during sampling has to be checked.
- Water is flushed through the coil for at least 10 minutes to be sure that the way is clean.
- A sample for H₂S is taken and the analysis made in the field. 5 ml NaOH solution 5 N is placed in 50 ml volumetric flask and filled to mark. This sample with NaOH is poured into an

Erlenmayer flask and 5 ml acetone added. Dithizone indicator is added and titrated with Hg acetate solution 0.001N using micrometer buret Gilmont. The concentration of H₂S is calculated in the field and later the same analysis is repeated in the laboratory and the results are compared (Paces, 1991).

- Samples are taken in air tight glass bulbs. At sampling the temperature of the water may not exceed 30°C
- The filter is connected with new filter paper inside (0.45 µm)
- The water flow is flushed through the filter for about 10 minutes. During that time the polyethylene bottles are marked and rinsed three times. The following bottles are used:
 - 3 bottles 100 ml Ru for SiO₂, Rd if it is necessary;
 - 2 bottles 500 ml Fu;
 - 2 bottles 500 ml Fa;
 - 1 bottle 100 ml Fa for stable isotopes;
 - 1 bottle 100 ml to analyse SO₄²⁻ with 2 ml 0.2 M ZnAc added to precipitate H₂S, Fp.
- The oxygen is measured by Chem-metrics ampules, first the range 0-100 ppb is tried and then if the concentration of oxygen is close to 0 more accurate: 0-10 ppb range issues
- Finally the temperature is measured
- The sampling apparatus is disconnected.

Analytical methods

Procedures for volatile constituents

Volatile constituents such as CO₂ and H₂S as well as pH must be measured soon after sample collection. Therefore, a description of analytical procedures for these elements is included (Trujillo et al., 1987).

Determination of pH and carbonate. The following equipment and reagents are needed:

- Portable pH meter
- pH electrode
- Reference electrode solution
- Three small beakers for pH buffers
- 150 ml beaker for sample
- 50 ml and 100 ml volumetric flasks
- Thermometer
- 25 ml or 50 ml burette calibrated at 0.1 ml intervals
- Burette stand and clamp
- 1 ml and 5 ml automatic pipettes
- 0.1 N HCl solution
- Approximately 0.1 N NaOH solution
- pH buffers (pH = 4; 7; 10)
- Distilled water

Total carbonate is determined by titration with 0.1 N HCl solution from pH = 8.2 to pH = 3.8 at about 20°C but pH is measured using a pH meter. The analytical procedure for water follows the next steps:

- Adjust the pH meter using the buffers
- Measure 50 ml of sample using the volumetric flask and put into the 150 ml beaker
- Determine the pH and temperature of the sample
- Adjust the pH carefully to pH = 8.2, using 0.1N HCl solution if the pH is higher than 8.2 or using 0.1N NaOH solution if the pH is lower than 8.2
- Titrate the sample from pH = 8.2 to pH = 3.8 using 0.1N HCl solution
- Record the amount of 0.1N HCl solution

The equation that is used for the calculation of the carbonate concentration is

$$\text{ppm } CO_2 = (88 \times \text{ml HCl}) - 7.92 - (1.182 \times \text{ppm } H_2S) - (0.0088 \times \text{ppm } SiO_2)$$

Determination of hydrogen sulfide by dithizone. The following equipment and reagents are needed:

- 10 ml burette calibrated at 0.05 ml intervals, burette stand and clamp or a 1 ml micro syringe
- 50 ml Erlenmayer flask
- Finnpiettes (0-200 μ l, 200-1000 μ l and 10000-5000 μ l)
- 10 ml measuring cylinder
- Acetone
- 5N NaOH solution
- Solid dithizone
- 0.001M α Hg(CH₃COO)₂ solution freshly prepared.

Hydrogen sulfide is determined by titration with α Hg(CH₃COO)₂ solution. The analytical procedure for water follows the next steps:

- 45 ml of sample is combined with 5 ml of 5N NaOH solution in a volumetric flask
- Measure 5 ml acetone into a 50 ml Erlenmayer flask
- Add the sample from step 1; the sample can be diluted if the H₂S concentration is high
- Add a small grain of solid dithizone
- Titrate with 0.001M α Hg(CH₃COO)₂ to red endpoint
- Record volume of sample and amount of α Hg(CH₃COO)₂ needed

The equation used for the calculation of the hydrogen sulfide concentration is

$$\text{ppm } H_2S = \frac{50}{45} \times \frac{\text{ml titer} \times 34}{\text{ml sample}}$$

During the titration a black precipitate of HgS forms. The endpoint is recorded when the colour changes from the yellow colour of the dithizone in alkaline solution to the red colour of the Hg-dithizonate. If the concentration of H₂S is high the sample becomes yellowish brown and even black during titration. This is caused by the HgS precipitate and makes the endpoint uncertain. In the case of high concentrations of H₂S, it is better to reduce the volume of the sample.

Spectrophotometric determination of silica

This method is based on the reaction of silica with molybdate ions at pH of 1.2-1.5; a yellow silicomolybdate complex is formed which is determined by spectrophotometry. If the concentration of silica in thermal water is higher than 100 ppm, the silica can polymerize and the polymerized silica will not react with molybdate. Treatment with alkali converts it all to the monomeric state.

As described under sample collection, it is desirable to dilute samples containing more than 100 ppm SiO₂ sufficiently to bring the final silica concentration below 100 ppm. When this is done, later analysis should follow the procedure described for samples containing less than 100 ppm SiO₂. Dilution below 100 ppm is necessary for saline waters as the salinity catalyses.

The adopted procedure covers the concentration range of 20-500 ppm. Higher concentrations can be determined by taking smaller aliquots. The main disadvantage of this method is the instability of colour of the solution. This necessitates that samples and standards need to be prepared at the same time and that absorption must be read 10-60 minutes after developing the colour.

No interference will occur from elements present in the thermal waters. Only colour or turbidity of the

sample will interfere. High concentrations of hydrogen sulphide may reduce the silicomolybdate complex to molybdenum blue. This can be prevented by oxidizing the sulphide with iodine.

The following equipment and reagents are used:

- Spectrophotometer Perkin Elmer with sipper cell
- 50 ml volumetric flasks
- Automatic pipettes
- HCl, solution; 6 N
- Ammonium hepta molybdate - tetra hydrate 10 % W/V
- Iodine, solution 0.1 N
- Sodium thiosulphate, solution 0.05 N
- Hot spring water from Spóastadir (102.8 ppm SiO₂).

The following procedure is used for calculating the silica concentration:

- From the stock Spóastadir water pipette 2.5, 5 and 10 mls into 50 ml volumetric flasks. This corresponds to 25.7-51.4 and 102.8 ppm SiO₂. A blank of deionized water should also be prepared in a 50 ml volumetric flask.
- 10 mls of sample is pipetted into a 50 ml volumetric flask.
- Iodine solution is added by drops to blank, standards and samples until yellow colour persists. Then sodiumthiosulphate is added by drops until the colour vanishes.
- Add approximately 20 mls of DI water to the flasks and 1 ml of 6N HCl, mix. Add 2 mls of the molybdate solution, mix. Fill the volumetric flasks to the mark with DI-water, mix and allow at least 10 minutes for colour development.
- Measure the absorption of blank, standards and samples of 410 nm.

Fluoride analysis

This method is based on electrode measurement. The fluoride electrode has a single-crystal lanthanum fluoride membrane and an internal reference. The membrane is an ionic conductor where only fluoride ions are mobile. Measurements are based on the development of a potential across this membrane when it is in contact with a solution containing free fluoride ions. This potential is compared to a constant external reference potential.

Equipment and reagents used for measuring the concentration of the fluoride:

- Orion Model 811 pH/millivolt meter
- Orion Fluoride Combination Electrode Model 96-09
- Magnetic stirrer
- Fluoride standard 1000 ppm concentration
- TISAB III.

For the analysis of the fluoride, first standard solutions: 0.1; 0.25; 0.5; 0.75; 1; 5 ppm F have to be prepared. The chosen concentrations of the standards depend on the approximate concentration of the samples. 20 ml standards and samples are measured and 2 ml TISAB III buffer added. The electrodes are placed in solution. The potential is measured for all standards. Then the potential for the samples is measured and then again for all standards for calculating an average value for standards. The linear equation of standards is calculated. Using a computer program the fluoride concentration in the samples is calculated.

The Mohr titration of chloride concentration

The reason for using the Mohr titration for analyse of chloride as well as ion-chromatography is that it is a simple method which is easily installed and does not require expensive equipment. It is also an excellent method for field labs.

Chloride is titrated with a silver-nitrate solution, using potassium chromate as an indicator. The colour changes from yellow to brown, but the colour change is very difficult to identify. The following solutions are used:

- Silver nitrate solution 0.0141 M; 2.395 g AgNO₃ are dissolved in water and diluted to 1000 ml
- Potassium chromate indicator 5%; 5 g K₂CrO₄ are dissolved in 100 ml of water
- Sodium hydroxide solution 1N; 20 g NaOH are dissolved in 500 ml of water

The blank (deionized water) and the standard are prepared. The concentration of the standard is 10 ppm chloride. The concentration in geothermal water is known to be between 1000 and 2000 ppm. 0.5 ml of geothermal water are taken and diluted to 100 ml. The analysed samples and a reference sample with a known concentration are prepared and then the blank, the standard, the samples and the reference sample are put into porcelain bowls. The pH is checked as it must be above 8.2. If it is not, 1N sodium hydroxide solution is added drop by drop. After this the titration with silver nitrate solution is started in the presence of the indicator (8 drops K₂CrO₄ in each solution). The titration is ready when the colour changes from yellow to brown. During the titration a magnetic stirrer is used. Due to the small amount of silver nitrate solution which is necessary for titration, it is better to use Gilmont micrometer buret than normal buret as it is easier to control. One untitrated blank is kept for comparison as well as another one titrated to the end point.

The following equation is used to calculate the concentration of chloride:

$$\text{ppm Cl} = \frac{\text{ml titer} - \text{ml blank}}{\text{ml sample}} \times 500$$

Sulphate concentration - analysis

The Thorin method is generally used instead of the ion-chromatography method due to the fact that it is easy and does not need special equipment. In most geothermal waters sulphate can conveniently be determined by titration with 0.005M barium perchlorate solution using thorin to detect the end point. The detection limit is 2 ppm. The equipment and reagents which are used are presented below:

- 25 ml burette with ionic exchange resin; the bottom of the burette should be plugged with a small piece of glass wool; about 15 ml of resin should be placed in the burette
- 10 ml burette for the standard barium perchlorate solution, calibrated at 0.02 ml intervals
- Magnetic stirrer
- 2 porcelain bowls
- Cation exchange resin
- 2-propanol, analytical reagent grade
- Perchloric acid, analytical reagent grade
- Absolute ethyl alcohol, analytical reagent grade
- Standard barium perchlorate solution 0.005M
- Standard sulphate solution 1000 ppm SO₄²⁻
- Thorin 0.2%

First the ionic exchange resin burette is filled with a sample and passed through the column. Then the burette is filled again with sample and this second aliquot passed through. The burette is filled for the third time and the water level adjusted to the zero mark. 10 ml of sample are passed dropwise through the burette (less volume if the sulphate concentration is high) and collected into a porcelain bowl. 40 ml of propanol and 3 drops of the thorin indicator solution are added and then titrated with the barium perchlorate solution until the first colour change from yellow to pink is observed. During the titration the solution is stirred continuously with the magnetic stirrer. The titer is recorded. The following equation is used for calculating the sulphate concentration:

$$\text{ppm } SO_4 = \frac{\text{ml } Ba(ClO_4)_2 \times N \times 96060}{\text{ml sample}}$$

All cations interfere by this method. In the resin the cations are exchanged for H^+ . For detection of an end point the pH of the solution must be in the range 2.5-3.5. Thus, saline waters which produce a pH of less than about 2.5 through ionic exchange in the resin cannot be analysed by this method.

Boron analysis - azomethine method

This method is based on the light absorption by a yellow colour complex formed when boron reacts with azomethine-H reagent in a special buffer solution. The following equipment and reagents are used:

- Spectrophotometer Perkin Elmer with sipper cell
- Polyethylene vials with caps, 50 ml capacity
- Pipettes: adjustable, with disposable tips, for preparing standards and transferring samples and reagents
- Buffer solution; pH 5.0 to 5.5
- Azomethine-H solution, this solution must rest for at least one hour
- Boron solution 1000 ppm.

Preparation of standards:

- A working standard is prepared by diluting a commercial stock solution (1000 ppm) to 10 ppm with deionized water and stored in a plastic container. There are necessary five standard solutions: 0.1; 0.25; 0.5; 0.75 and 1 ppm B.
- In vials there are put 4 ml of four blanks, 3 standards 0.1 ppm B, 3 standards 0.25 ppm B, 2 standards 0.5 ppm B, 2 standards 0.75 ppm B, 2 standards 1 ppm B, 2 samples from well 04, 2 samples from well 12 and 2 reference samples.
- Then there are added 4 ml buffer, 2 ml azomethine solution in each vial
- The vials are stopped, the contents are shaken. The vials last 30 minutes and then the blanks, standards and samples are read at the same time at the spectrophotometer at 420 nm.
- The calibration curve is made by plotting the absorption readings of the standards, respectively, against the concentrations; a computer program is also available to make calibration curves which may also be used.
- Boron concentration is calculated graphically using the calibration plot or is done by a computer using a linear regression program.

Sodium, potassium, magnesium, calcium - atomic absorption, direct aspiration analysis

For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by contributing contaminants through leaching or surface desorption and by depleting concentrations through adsorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention.

For the determination of dissolved constituents the sample must be filtered through a 0.45 μm membrane filter as soon as practical after collection. The filtrate is acidified with suprapure HNO_3 . Normally 4 ml of acid per liter should be sufficient to preserve the sample.

Preparation of standard solutions:

It is necessary to prepare at least 3 stock solutions, starting by standard solutions with the concentration of 1000 ppm. If possible the most dilute standard should have less absorption than the samples measured and the most concentrated standard more absorption than the samples.

Preparation of Cs - La solution:

First 58.64 g of lanthanum oxide are mixed with 50 ml of deionized water and then slowly and cautiously 250 ml of concentrated HCl are added to dissolve the La_2O_3 . Then 12.67 g CsCl is dissolved in deionized water. The two solutions obtained are combined and diluted to 1 l with deionized water. The Cs-La solution is added in all the plastic bottles, containing the standard solutions and the samples. Ionization should be controlled by the addition of mixture, and oxysalt interference on Calcium is reduced. 1 ml Cs-La solution is added to each 10 ml standard and samples. There is also a blank to which is added Cs-La solution.

After choosing the proper hollow cathode lamp for analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period it is necessary to align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width and adjust the hollow cathode current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flowrate for maximum percent absorption and stability and balance the photometer. A series of standards are run of the element under analysis and a calibration curve is constructed by plotting the concentrations of the standards against the absorption. The curve corrector is set to read out the proper concentration. The samples are aspirated and the concentrations are determined directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

APPENDIX III: WATCH calculations on the 1972, 1984 and 1991 water samples from well SN-4, Seltjarnarnes

ICELANDIC WATER CHEMISTRY GROUP

Program WATCH, version 2.1 / 1994

oana analysis

1972 Seltjarnarnes

Water sample (mg/kg)	Steam sample				
pH/deg.C	8.30/ 23.0	Gas (volume %)		Reference temperature	deg.C : 111.5 (Chalcedony)
CO2	19.00	CO2	.00	Sampling pressure	bar abs. : 1.0
H2S	.00	H2S	.00	Discharge enthalpy	kJ/kg : 468. (Calculated)
NH3	.00	NH3	.00	Discharge	kg/s : .0
B	.00	H2	.00	Steam fraction at collection	: .0000
SiO2	105.50	O2	.00	Measured temperature	deg.C : 116.0
Na	325.00	CH4	.00		
K	6.70	N2	.00		
Mg	.100				
Ca	116.00	Liters gas per kg		Condensate (mg/kg)	
F	1.000	condensate/deg.C	.00/ .0	pH/deg.C	.00/ .0
Cl	542.00			CO2	.00
SO4	203.50	Total steam (mg/kg)		H2S	.00
Al	.0000	CO2	.00	NH3	.00
Fe	.0000	H2S	.00	Na	.00
TDS	1366.00	NH3	.00		

Ionic strength = .02434

Ionic balance : Cations (mol.eq.) = .01970999 Anions (mol.eq.) = .01967577 Difference (%) = .17

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-16.795	99.999	Albite, low	-16.095	99.999	Analcime	-12.910	99.999
Anhydrite	-5.772	-5.993	Calcite	-9.641	-9.250	Chalcedony	-2.753	-2.772
Mg-Chlorite	-80.056	99.999	Fluorite	-10.527	-11.619	Goethite	-4.241	99.999
Laumontite	-26.674	99.999	Microcline	-18.093	99.999	Magnetite	-28.825	99.999
Ca-Montmor.	-82.968	99.999	K-Montmor.	-40.233	99.999	Mg-Montmor.	-84.170	99.999
Na-Montmor.	-40.281	99.999	Muscovite	-20.517	99.999	Prehnite	-36.437	99.999
Pyrrhotite	-94.068	99.999	Pyrite	-138.698	99.999	Quartz	-2.996	-2.772
Wairakite	-24.443	99.999	Wollastonite	10.482	9.037	Zoisite	-35.656	99.999
Epidote	-42.678	99.999	Marcasite	-115.950	99.999	Talc	14.894	15.428
Chrysotile	22.736	20.972	Sil. amorph.	-2.159	-2.772			

1972 Aquifer liquid cooled to 90.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-17.632	99.999	Albite, low	-16.859	99.999	Analcime	-13.478	99.999
Anhydrite	-5.467	-5.923	Calcite	-9.272	-9.017	Chalcedony	-2.922	-2.771
Mg-Chlorite	-80.616	99.999	Fluorite	-10.556	-11.580	Goethite	-5.041	99.999
Laumontite	-27.678	99.999	Microcline	-19.081	99.999	Magnetite	-30.464	99.999
Ca-Montmor.	-88.132	99.999	K-Montmor.	-43.045	99.999	Mg-Montmor.	-89.231	99.999
Na-Montmor.	-43.023	99.999	Muscovite	-21.778	99.999	Prehnite	-37.142	99.999
Pyrrhotite	-104.804	99.999	Pyrite	-154.380	99.999	Quartz	-3.198	-2.771
Wairakite	-24.987	99.999	Wollastonite	11.140	9.320	Zoisite	-36.166	99.999
Epidote	-44.415	99.999	Marcasite	-130.306	99.999	Talc	16.269	16.382
Chrysotile	24.496	21.924	Sil. amorph.	-2.272	-2.771			

1972 Aquifer liquid cooled to 70.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-18.565	99.999	Albite, low	-17.711	99.999	Analcime	-14.120	99.999
Anhydrite	-5.205	-5.871	Calcite	-8.971	-8.808	Chalcedony	-3.099	-2.770
Mg-Chlorite	-81.539	99.999	Fluorite	-10.622	-11.550	Goethite	-5.747	99.999
Laumontite	-28.831	99.999	Microcline	-20.171	99.999	Magnetite	-31.988	99.999
Ca-Montmor.	-94.181	99.999	K-Montmor.	-46.309	99.999	Mg-Montmor.	-95.165	99.999
Na-Montmor.	-46.207	99.999	Muscovite	-23.249	99.999	Prehnite	-38.065	99.999
Pyrrhotite	-114.841	99.999	Pyrite	-169.570	99.999	Quartz	-3.406	-2.770
Wairakite	-25.669	99.999	Wollastonite	11.828	9.683	Zoisite	-36.909	99.999
Epidote	-46.048	99.999	Marcasite	-144.110	99.999	Talc	17.709	17.563
Chrysotile	26.360	23.104	Sil. amorph.	-2.389	-2.770			

1972 Aquifer liquid cooled to 50.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-19.664	99.999	Albite, low	-18.715	99.999	Analcime	-14.883	99.999
Anhydrite	-4.966	-5.829	Calcite	-8.720	-8.603	Chalcedony	-3.297	-2.769
Mg-Chlorite	-82.885	99.999	Fluorite	-10.737	-11.526	Goethite	-6.429	99.999
Laumontite	-30.213	99.999	Microcline	-21.446	99.999	Magnetite	-33.553	99.999
Ca-Montmor.	-101.365	99.999	K-Montmor.	-50.170	99.999	Mg-Montmor.	-102.214	99.999
Na-Montmor.	-49.974	99.999	Muscovite	-25.002	99.999	Prehnite	-39.270	99.999
Pyrrhotite	-125.035	99.999	Pyrite	-185.595	99.999	Quartz	-3.632	-2.769
Wairakite	-26.535	99.999	Wollastonite	12.603	10.160	Zoisite	-37.927	99.999
Epidote	-47.739	99.999	Marcasite	-158.572	99.999	Talc	19.326	19.080
Chrysotile	28.483	24.619	Sil. amorph.	-2.521	-2.769			

1972 Aquifer liquid cooled to 30.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-20.950	99.999	Albite, low	-19.889	99.999	Analcime	-15.778	99.999
Anhydrite	-4.757	-5.799	Calcite	-8.528	-8.402	Chalcedony	-3.522	-2.769
Mg-Chlorite	-84.696	99.999	Fluorite	-10.912	-11.509	Goethite	-7.111	99.999
Laumontite	-31.845	99.999	Microcline	-22.925	99.999	Magnetite	-35.222	99.999
Ca-Montmor.	-109.392	99.999	K-Montmor.	-54.493	99.999	Mg-Montmor.	-110.080	99.999
Na-Montmor.	-54.178	99.999	Muscovite	-26.986	99.999	Prehnite	-40.778	99.999
Pyrrhotite	-135.548	99.999	Pyrite	-202.813	99.999	Quartz	-3.872	-2.769
Wairakite	-27.596	99.999	Wollastonite	13.482	10.772	Zoisite	-39.238	99.999
Epidote	-49.684	99.999	Marcasite	-174.015	99.999	Talc	21.138	20.983
Chrysotile	30.911	26.520	Sil. amorph.	-2.670	-2.769			

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1984 Seltjarnarnes

Water sample (mg/kg)		Steam sample			
pH/deg.C	8.43/ 22.0	Gas (volume %)		Reference temperature	deg.C : 105.9 (Chalcedony)
CO2	8.83	CO2	.00	Sampling pressure	bar abs. : 1.0
H2S	.00	H2S	.00	Discharge enthalpy	kJ/kg : 444. (Calculated)
NH3	.00	NH3	.00	Discharge	kg/s : .0
B	.22	H2	.00	Steam fraction at collection	: .0000
SiO2	96.55	O2	.00		
Na	442.51	CH4	.00	Measured temperature	deg.C : 115.3
K	11.55	N2	.00		
Mg	.088			Condensate (mg/kg)	
Ca	260.01	Liters gas per kg		pH/deg.C	.00/ .0
F	.685	condensate/deg.C	.00/ .0	CO2	.00
Cl	972.50			H2S	.00
SO4	232.73	Total steam (mg/kg)		NH3	.00
Al	.034	CO2	.00	Na	.00
Fe	.000	H2S	.00		
TDS	2257.00	NH3	.00		

Ionic strength = .04008
 Ionic balance : Cations (mol.eq.) = .03181564 Anions (mol.eq.) = .03188502 Difference (%) = -.22

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-16.997	-18.065	Albite, low	-16.279	-16.242	Analcime	-13.046	-13.431
Anhydrite	-5.691	-5.729	Calcite	-9.541	-9.273	Chalcedony	-2.795	-2.811
Mg-Chlorite	-80.161	-88.289	Fluorite	-10.531	-11.663	Goethite	-4.453	99.999
Laumontite	-26.913	-25.812	Microcline	-18.332	-18.065	Magnetite	-29.252	99.999
Ca-Montmor.	-84.178	-90.911	K-Montmor.	-40.895	-47.803	Mg-Montmor.	-85.355	-94.248
Na-Montmor.	-40.926	-45.980	Muscovite	-20.814	-20.481	Prehnite	-36.593	-35.150
Pyrrhotite	-96.855	99.999	Pyrite	-142.718	99.999	Quartz	-3.046	-2.811
Wairakite	-24.566	-25.812	Wollastonite	10.646	9.376	Zoisite	-35.761	-36.358
Epidote	-43.126	99.999	Marcasite	-119.641	99.999	Talc	15.235	15.304
Chrysotile	23.171	20.927	Sil. amorph.	-2.187	-2.811			

1984

Aquifer liquid cooled to 90.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.	Theor.	Calc.	Theor.	Calc.		
Adularia	-17.632	-18.058	Albite, low	-16.859	-16.235	Analcime	-13.478	-13.424
Anhydrite	-5.467	-5.671	Calcite	-9.272	-9.066	Chalcedony	-2.922	-2.812
Mg-Chlorite	-80.616	-89.122	Fluorite	-10.556	-11.635	Goethite	-5.041	99.999
Lamontite	-27.678	-25.786	Microcline	-19.081	-18.058	Magnetite	-30.464	99.999
Ca-Montmor.	-88.132	-89.286	K-Montmor.	-43.045	-46.996	Mg-Montmor.	-89.231	-92.604
Na-Montmor.	-43.023	-45.174	Muscovite	-21.778	-20.206	Prehnite	-37.142	-35.364
Pyrrhotite	-104.804	99.999	Pyrite	-154.380	99.999	Quartz	-3.188	-2.812
Wairakite	-24.987	-25.786	Wollastonite	11.140	9.645	Solite	-36.166	-36.438
Epidote	-44.415	99.999	Marcasite	-130.306	99.999	Talc	16.269	16.170
Chrysotile	24.496	21.794	Stl. amorph.	-2.272	-2.812			

1984

Aquifer liquid cooled to 70.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.	Theor.	Calc.	Theor.	Calc.		
Adularia	-18.565	-18.049	Albite, low	-17.711	-16.227	Analcime	-14.120	-13.415
Anhydrite	-5.205	-5.609	Calcite	-8.971	-8.818	Chalcedony	-3.099	-2.812
Mg-Chlorite	-81.539	-90.325	Fluorite	-10.622	-11.605	Goethite	-5.747	99.999
Lamontite	-28.831	-25.757	Microcline	-20.171	-18.049	Magnetite	-31.988	99.999
Ca-Montmor.	-94.181	-87.045	K-Montmor.	-46.309	-45.882	Mg-Montmor.	-95.165	-90.337
Na-Montmor.	-46.207	-44.060	Muscovite	-23.249	-19.828	Prehnite	-38.065	-35.675
Pyrrhotite	-114.841	99.999	Pyrite	-169.570	99.999	Quartz	-3.406	-2.812
Wairakite	-25.669	-25.757	Wollastonite	11.828	10.066	Solite	-36.909	-36.564
Epidote	-46.048	99.999	Marcasite	-144.110	99.999	Talc	17.709	17.509
Chrysotile	26.360	23.133	Stl. amorph.	-2.389	-2.812			

1984

Aquifer liquid cooled to 50.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.	Theor.	Calc.	Theor.	Calc.		
Adularia	-19.664	-18.042	Albite, low	-18.715	-16.221	Analcime	-14.883	-13.409
Anhydrite	-4.966	-5.559	Calcite	-8.720	-8.581	Chalcedony	-3.297	-2.812
Mg-Chlorite	-82.885	-91.771	Fluorite	-10.737	-11.581	Goethite	-6.429	99.999
Lamontite	-30.213	-25.733	Microcline	-21.446	-18.042	Magnetite	-32.553	99.999
Ca-Montmor.	-101.365	-84.503	K-Montmor.	-50.170	-44.634	Mg-Montmor.	-102.214	-87.772
Na-Montmor.	-49.974	-42.793	Muscovite	-23.202	-19.404	Prehnite	-39.210	-36.047
Pyrrhotite	-125.024	92.999	Pyrite	-185.285	19.292	Quartz	-3.632	-2.812
Wairakite	-25.535	-23.723	Wollastonite	12.605	10.394	Solite	-37.927	-36.727
Epidote	-49.729	69.999	Marcasite	-159.202	99.999	Talc	19.326	19.163
Chrysotile	29.483	24.787	Stl. amorph.	-2.521	-2.812			

1984

Aquifer liquid cooled to 30.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.	Theor.	Calc.	Theor.	Calc.		
Adularia	-20.720	-18.026	Albite, low	-19.809	-16.215	Analcime	-15.778	-13.403
Anhydrite	-4.786	-5.323	Calcite	-8.328	-8.357	Chalcedony	-3.522	-2.812
Mg-Chlorite	-84.786	-93.523	Fluorite	-10.932	-11.564	Goethite	-7.111	99.999
Lamontite	-21.885	-23.315	K-Microcline	-22.255	-18.026	Magnetite	-35.222	99.999
Ca-Montmor.	-109.376	-81.305	K-Montmor.	-54.483	-43.125	Mg-Montmor.	-110.080	-84.768
Na-Montmor.	-54.148	-41.989	Muscovite	-26.986	-18.904	Prehnite	-40.778	-36.507
Pyrrhotite	-135.148	91.999	Pyrite	-202.083	19.999	Quartz	-3.872	-2.812
Wairakite	-27.428	-23.982	Wollastonite	13.402	11.245	Solite	-39.238	-36.939
Epidote	-49.684	29.999	Marcasite	-174.015	99.999	Talc	21.138	21.173
Chrysotile	30.911	26.797	Stl. amorph.	-2.670	-2.812			

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data

analysis

1991

Seltjarnarnes

Water sample (mg/kg)	Steam sample	Reference temperature	deg.C :	110.8	(Chalcedony)
PH/deg.C	8.49/ 24.6	Gas (volume %)			
CO2	10.90	CO2	.00		
H2S	.04	H2S	.00	Sampling pressure	bar abs. : 1.0
NH3	.00	NH3	.00	Discharge enthalpy	KJ/Kg : 465. (calculated)
B	.23	B2	.00	Discharge	Kg/s : .0
SiO2	106.00	O2	.00	Steam fraction at collection	: .0000
K	604.60	CH4	.00		
Na	14.41		.00	Measured temperature	deg.C : 112.8
Mg	510				
Ca	481.90	Liters gas per Kg condensate/deg.C	.00/	.0	
F	.642				
Cl	1581.00	Total steam (mg/kg)	.00		
SO4	278.00	CO2	.00		
AL	.023	H2S	.00		
Fe	.000	NH3	.00		
TDS	3550.00	NH3	.00		

Ionic strength = .06342
 Cations (mol.eq.) = .04957667
 Anions (mol.eq.) = .04961472
 Difference (%) = -.08

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-16.819	-18.077	Albite, low	-16.117	-16.214	Analcime	-12.926	-13.437
Anhydrite	-5.762	-5.576	Calcite	-9.629	-9.007	Chalcedony	-2.758	-2.777
Mg-Chlorite	-80.067	-83.836	Fluorite	-10.528	-11.552	Goethite	-4.267	99.999
Laumontite	-83.110	-94.212	Microcline	-18.121	-18.077	Magnetite	-28.877	99.999
Ca-Montmor.	-40.357	-47.623	K-Montmor.	-40.311	-49.487	Mg-Montmor.	-84.309	-97.031
Na-Montmor.	-94.406	99.999	Muscovite	-20.552	-21.143	Prehnite	-36.455	-34.732
Pyrrhotite	-42.457	-25.840	Pyrite	-139.184	99.999	Quartz	-3.002	-2.777
Wairakite	-42.732	99.999	Wollastonite	-10.502	9.751	Zoisite	-35.667	-36.265
Epidote	-22.788	23.571	Sil. amorph.	-2.163	-2.777	Talc	14.935	18.017

1991

Aquifer liquid cooled to 90.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-17.632	-18.067	Albite, low	-16.859	-16.204	Analcime	-13.478	-13.426
Anhydrite	-5.467	-5.488	Calcite	-9.272	-8.716	Chalcedony	-2.922	-2.778
Mg-Chlorite	-80.616	-84.884	Fluorite	-10.556	-11.513	Goethite	-5.041	99.999
Laumontite	-27.678	-25.806	Microcline	-19.081	-18.067	Magnetite	-30.444	99.999
Ca-Montmor.	-89.132	-92.186	K-Montmor.	-43.045	-48.480	Mg-Montmor.	-89.231	-94.985
Na-Montmor.	-43.023	-46.616	Muscovite	-21.778	-20.798	Prehnite	-37.142	-34.993
Pyrrhotite	-104.804	99.999	Pyrite	-154.380	99.999	Quartz	-3.198	-2.778
Wairakite	-24.987	-25.806	Wollastonite	-11.140	10.104	Zoisite	-36.166	-36.368
Epidote	-44.415	99.999	Marcasite	-130.306	99.999	Talc	16.269	19.138
Chrysotile	24.496	24.693	Sil. amorph.	-2.272	-2.778			

1991

Aquifer liquid cooled to 70.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-18.565	-18.058	Albite, low	-17.711	-16.195	Analcime	-14.120	-13.417
Anhydrite	-5.205	-5.417	Calcite	-8.971	-8.454	Chalcedony	-3.099	-2.778
Mg-Chlorite	-83.539	-86.077	Fluorite	-10.622	-11.480	Goethite	-5.747	99.999
Laumontite	-28.831	-25.776	Microcline	-20.171	-18.058	Magnetite	-31.988	99.999
Ca-Montmor.	-94.181	-89.987	K-Montmor.	-46.309	-47.385	Mg-Montmor.	-95.165	-92.766
Na-Montmor.	-46.207	-45.522	Muscovite	-23.249	-20.425	Prehnite	-38.065	-35.294
Pyrrhotite	-114.841	99.999	Pyrite	-169.570	99.999	Quartz	-3.406	-2.778
Wairakite	-25.669	-25.776	Wollastonite	-11.828	10.534	Zoisite	-36.909	-36.478
Epidote	-46.048	99.999	Marcasite	-144.110	99.999	Talc	17.709	20.486
Chrysotile	26.360	26.042	Sil. amorph.	-2.389	-2.778			

1991

Aquifer liquid cooled to 50.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-19.664	-18.050	Albite, low	-18.715	-16.187	Analcime	-14.881	-13.409
Anhydrite	-4.966	-5.360	Calcite	-8.720	-8.208	Chalcedony	-3.297	-2.778
Mg-Chlorite	-82.895	-87.526	Fluorite	-10.737	-11.454	Goethite	-6.429	99.999
Laumontite	-30.213	-25.751	Microcline	-21.446	-18.050	Magnetite	-33.553	99.999
Ca-Montmor.	-101.365	-87.458	K-Montmor.	-50.170	-46.125	Mg-Montmor.	-102.214	-80.218
Na-Montmor.	-49.974	-44.258	Muscovite	-25.002	-19.999	Prehnite	-39.270	-35.661
Pyrrhotite	-125.035	99.999	Pyrite	-185.595	99.999	Quartz	-3.632	-2.778
Wairakite	-22.535	-25.751	Wollastonite	-12.603	11.066	Zoisite	-37.927	-36.636
Epidote	-47.739	99.999	Marcasite	-158.572	99.999	Talc	19.326	22.139
Chrysotile	28.483	27.696	Sil. amorph.	-2.521	-2.778			

1991

Aquifer liquid cooled to 30.0 °C

Log solubility products of minerals in deep water

	Theor.	Calc.		Theor.	Calc.		Theor.	Calc.
Adularia	-20.950	-18.042	Albite, low	-19.889	-16.181	Analcime	-15.778	-13.403
Anhydrite	-4.757	-5.317	Calcite	-8.588	-7.979	Chalcedony	-3.522	-2.778
Mg-Chlorite	-84.696	-89.334	Fluorite	-10.912	-11.436	Goethite	-7.111	99.999
Laumontite	-31.845	-25.732	Microcline	-22.925	-18.042	Magnetite	-35.222	99.999
Ca-Montmor.	-109.392	-84.467	K-Montmor.	-54.493	-44.632	Mg-Montmor.	-110.080	-87.211
Na-Montmor.	-54.178	-42.770	Muscovite	-26.986	-19.498	Prehnite	-40.778	-36.119
Pyrrhotite	-135.548	99.999	Pyrite	-202.813	99.999	Quartz	-3.972	-2.778
Wairakite	-27.596	-25.732	Wollastonite	-13.482	11.717	Zoisite	-39.238	-36.847
Epidote	-49.684	99.999	Marcasite	-174.015	99.999	Talc	21.138	24.142
Chrysotile	30.911	29.698	Sil. amorph.	-2.670	-2.778			