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**SCALING AND CORROSION POTENTIAL OF
SELECTED GEOTHERMAL WATERS IN SERBIA**

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ABSTRACT

A study of scaling and corrosion potential of selected geothermal waters in Serbia is presented in this report. ReInjection will be an integral part of the design for any future geothermal development in Serbia. Two of the important problems in connection with reInjection are scaling and corrosion, since the chemicals dissolved in geothermal waters may have a tendency to precipitate or cause corrosion in a reInjection well. The selected geothermal waters are characterized by a wide range of temperatures (25-94°C), are mainly of the sodium-bicarbonate type, with important amounts of calcium ions as well as dissolved carbon dioxide. Therefore they are prone to calcite scale deposition.

With the aqueous speciation computer programme WATCH, different thermal and chemical conditions can be simulated and the resulting changes in water chemistry predicted. The results show that geothermal waters in Serbia are slightly supersaturated with respect to calcium carbonate. After adiabatic boiling the extent of supersaturation increases significantly. Heating of spent geothermal waters from 25°C to the production well discharge temperature or the predicted chalcedony geothermometer temperature gives rise to a slight calcite supersaturation.

Some of the geothermal waters have a significant corrosion potential. Their carbon dioxide and oxygen concentrations are high. These two parameters are of the greatest importance from the point of view of corrosion in geothermal systems. The ferrous ion is the stable form of iron in geothermal waters. Therefore corrosion would be expected to proceed when iron comes into contact with the above dissolved gases. These results agree with those of several reInjection tests in Serbia during the past few years.

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1. INTRODUCTION

"Like all other sources of energy, geothermal has its own problems in production, transmission, distribution and utilization. One of them is deposition of solids in the system, from the geothermal fluid" (Bjornsson, 1989). Another problem is corrosion.

Hydrogeochemistry has wide applications in reservoir engineering and plays an important role in the assessment of a geothermal resource for production and development of geothermal energy. Engineers who design casings, pipelines and power plants must have knowledge of the chemical characteristics of the production fluid that may cause difficulties during development. Fluid chemistry provides them with information concerning the potential for scaling and corrosion (Janik, 1985).

Scaling and corrosion have presented problems in many geothermal systems. Dissolved materials in geothermal waters can exhibit aggressive corrosive properties or have the tendency to deposit large amounts of mineral scale. Either property can seriously shorten the life of pipes in the production well or the reinjection well. Scaling and corrosion constitute technical barriers to the utilization of geothermal resources and we can say that these are two of the more important geothermal utilization problems that require the close attention of chemists and geologists.

The composition of the geothermal fluid results from the environment from which it is extracted. The history of the fluid as it comes into contact with various minerals is the key to understanding the tendency of these fluids to promote scaling and corrosion and, as a consequence, making rational material selections for construction. The corrosion and scaling problems encountered in geothermal systems are a direct result of geochemical changes that occur in the water (Miller, 1980).

Calcium and carbon dioxide rich water at a temperature of about 30°C has been subjected to a few reinjection tests during the past five years in Serbia. In all tests the injected water has been supersaturated with many minerals, including calcite.

The selected geothermal waters from Serbia are characterized by a wide range of temperature (25 to 94°C). These geothermal waters are of the sodium-bicarbonate type, with important amounts of calcium ions and carbon dioxide. Their dissolved solids concentration is up to 10 g/l.

Water-rock interaction has been approached using the aqueous speciation computer programme WATCH (Arnorsson et al., 1982), to determine which minerals exert a control on the fluid chemistry at downhole and surface conditions. Prior to computing the degree of saturation of the fluid with respect to selected minerals, we had to choose the degree of degassing as well as the reference temperatures. The results of these computations show equilibrium conditions of geothermal waters with respect to calcium carbonate as well as other minerals.

Carbonate scale has been encountered in low temperature systems in which waters are allowed to degas and those from different temperature aquifers that are allowed to mix (cold injection water and hot aquifer water). With the computer programme WATCH we can simulate thermal and chemical conditions during reentry into the aquifer and predict changes in water chemistry and processes in the reservoir resulting from the injection of waters having known concentrations of dissolved solids. The reinjection of geothermal water is a delicate operation as far as chemistry is concerned. Geothermal water (after degassing) is usually supersaturated with respect to calcite and other minerals. Of course, the best "chemical method" to prevent precipitation in pipes, wells or in the reservoir is to reinject the water without exposing it to air. But this method delays

rather than prevents the precipitation.

Geothermal waters can reach a state of chemical nonequilibrium during the energy extraction process because of temperature and/or pressure changes. As the water attains equilibrium, precipitates, that can plug the injection flow, form. The precipitation of calcite is typically a production problem, although it may result from the injection of incompatible waters as they are reheated. Injection reservoir temperatures are generally higher than the temperatures of the spent geothermal waters, and the injected waters may become reheated upon entering the reservoir. This increase in water temperature can cause scaling minerals with retrograde solubility (calcite). When carbon dioxide is lost, *pH* shifts toward more basic, scale-forming conditions. If calcium carbonate is close to its solubility limit in the cooled geothermal water (spent geothermal water) it may exceed its solubility limit as it is reheated during reinjection. The correct approach is to use hydrochemical models to verify the compatibility of the fluid for the expected range of operating temperatures.

Hydrochemical modeling may be used to identify chemical problems arising from injecting water into a geothermal reservoir. The chemical incompatibility that results from differences in chemical composition and temperature may cause the precipitation of calcite. The scaling tendency of geothermal water can be calculated, but not the kinetics of scale deposition (for example, the deposition rate can be very rapid during calcite precipitation). Hydrochemical models use the principles of thermodynamics to calculate the tendency of reactions to take place as a system proceeds toward equilibrium. These models can also predict the effects of temperature and pressure on precipitation reactions.

Equilibrium calculations generally show that geothermal waters are saturated with respect to calcite and that changes in saturation occur upon cooling, heating and degassing. These calculations, based on the WATCH aqueous speciation programme, have been used to estimate whether the water is saturated with respect to calcite and whether supersaturation occurs upon boiling and heating.

Calcite scaling is one of the most persistent problems in the exploitation of geothermal energy. Calcite becomes more soluble at lower temperatures. Because of this there should be no problem with calcite deposition when a geothermal well is discharged and the temperature is lowered. This is the case where the water is conductively cooled without steam formation. When flashing takes place, carbon dioxide is distributed into steam and the *pH* changes favouring the carbonate ions. The concentration of calcium ions increases as well, and thus the calcite deposition potential is increased.

The chemical composition of water collected at the wellhead is read into the WATCH programme and it was used to calculate the solubility products of several minerals as well as the effect of degassing. By changing the reference temperature the effect of heating (during reinjection) or cooling on solubility products is studied. The WATCH programme assumes that steam has been separated before sampling and that the composition represents water phase only. By application of the WATCH programmes the effect of change in chemical composition on the stability of the processed water is studied. These changes could be caused by the deposition of solids, injection of chemicals or mixing of waters with different chemical compositions.

2. SCALING

2.1 General

Water is always in the process of dissolving or depositing solids - scale (incrustation, fouling, deposits etc.). Today we know that the extent of mineral scaling from a water is not wholly dependent upon the water itself, or its dissolved ion content. The extent of mineral scales are dependent upon the degree of supersaturation of the water with respect to a particular mineral, the rate of temperature change and changes in the pressure as well as the *pH* of the water. Thus where water is used, one can expect a variety of potential deposition problems. Water is a universal solvent, since almost everything is soluble in it to some extent. This fact, as well as definite solubility limits, results in water's ability to dissolve and deposit minerals. Figure 1 is a schematic diagram of these processes.

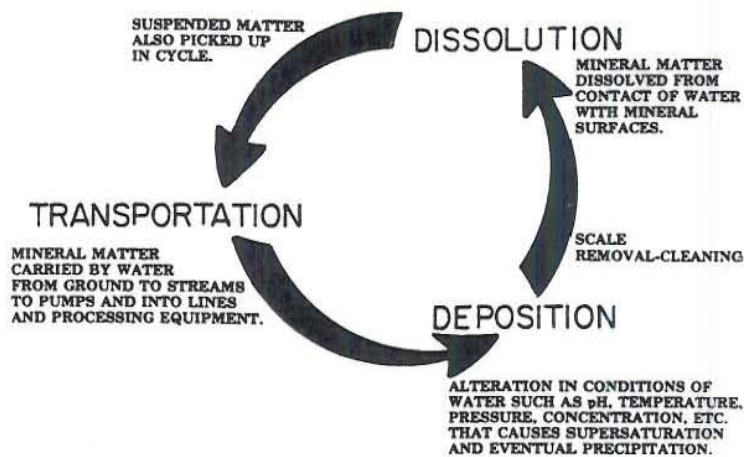


FIGURE 1: The scaling process (Cowan and Weintritt, 1976)

The solubility of a given mineral in water is controlled by variations in temperature, pressure, *pH*, redox potential and the relative concentrations of other substances in solution. The gas content of water can vary considerably due to its entry from the surface into an aquifer, the dissolution of other constituents and changes in pressure. An increase in the partial pressure of gases in contact

with water, increases the solubility of gases in water which in turn may increase or decrease the mobility of some other constituents. Oxygen decreases the mobility of iron, while carbon dioxide increases the mobility of many constituents of which calcium is the most important. Hydrogen sulphide and carbon dioxide occur in variable amounts in geothermal waters. However oxygen plays a significant role in the formation of iron compound deposits from geothermal waters in surface equipment. Natural waters commonly contain dissolved carbon dioxide gas. Large concentrations of carbon dioxide, particularly at the pressure encountered in deep wells, are converted to carbonic acid. This causes a decrease in the *pH* of the water. Iron is present in practically all rocks and is usually dissolved in groundwater in the form of bicarbonate. Upon exposure to air, soluble ferrous iron oxidizes to insoluble or colloidal ferric iron. A deposit that may undergo further oxidation is formed (Cowan and Weintritt, 1976).

2.2 Literature review

The main source for this chapter of the report are papers presented at the International workshop on deposition of solids in geothermal systems, Reykjavik, 1988 (Editors: Gundmundsson and Thomas, 1989).

At each stage of the geothermal utilization process, the natural hydrothermal fluids that may have been at thermal and chemical equilibrium with heated reservoir rocks can be exposed to

substantial changes in temperature and pressure, which can affect the solubility of a variety of dissolved mineral species. The lowering of the fluid temperature can decrease the solubility of metal sulphide species and allow them to precipitate individually or together. Changes in fluid pressure can allow a phase change to take place: either boiling or exsolution of dissolved gases. Loss of dissolved gases (carbon dioxide or hydrogen sulphide) from the geothermal water can also drastically affect the pH , and therefore the solubility of both calcium carbonate and sulphide minerals.

In intermediate and low temperature geothermal systems calcium carbonate scale has been reported by a few authors. Vuataz et al. (1989) have dealt with calcite saturated waters in the sandstone aquifer at Melleray, France, where a combination of sulphide and calcite scale was responsible for the deterioration of reinjection well permeability. Kristmannsdottir (1989) also notes that calcite scale has been encountered in low temperature systems in Iceland when fluids are allowed to degas and, on occasion, when fluids of different temperatures, or salinities are allowed to mix. Prevention of scale deposition in low temperature systems is typically controlled by limiting the extent of degassing and the resultant pH changes that bring about the supersaturation of carbonate minerals.

Mixed metal sulphide and oxide deposition has been reported in virtually every type of geothermal system including those of low and intermediate enthalpy. Criaud and Fouillac (1989) note that low enthalpy fluids with high concentrations of dissolved solids can cause severe corrosion of steel production casings. The iron liberated by corrosion reacts rapidly with sulphide-rich geothermal fluids and can cause higher deposition rates of metal sulphide scale than is typically found in higher temperature environments. Ungemach and Roque (1988) and Honegger et al. (1989) found that corrosion of mild steel production casing results in the deposition of large quantities of iron sulphide scale in both the production and reinjection wells. The iron phases identified include pyrite, pyrrhotite, and iron carbonate. The mechanism of corrosion attack has not been unequivocally identified, but theoretically possible processes include chemical attack by hydrogen sulphide and carbon dioxide, bacterial attack and galvanic attack.

Other modelling efforts include investigations of solid deposits from fluids that were to be injected into geothermal reservoirs. Crecraft and Koenig (1989) presented the results of chemical modelling that was performed for the sequence of processes undergone by the injectate as it encountered changing thermal and chemical conditions during its reentry into the reservoir.

The precipitation of dissolved solids from geothermal fluids is a virtually ubiquitous phenomenon which takes place in geothermal fluids at a different chemical composition over a wide range of temperatures. Moreover, the precipitation of solids from natural fluids is a highly complex physical and chemical process that is still poorly understood and over which we have only limited control (Thomas and Gudmundsson, 1989).

Arnorsson (1989) reviewed theoretical considerations that apply to the deposition of calcium carbonate minerals from geothermal waters. Studies of geothermal fluid chemistry in different parts of the world indicate that the waters at depth in the reservoir are very close to being calcite saturated. Figure 2 shows the state of calcite saturation for selected Icelandic geothermal waters. Calcite undersaturation may exist in some fields, probably due to an insufficient supply of carbon dioxide to the system. The ratio of the calcium ion activity and the hydrogen ion activity squared in geothermal waters tends to vary inversely with temperature for many fields (Figure 3). The reason is that it is controlled by a mineral buffer. It is evident that this buffer, together with calcite, will fix the partial pressure of carbon dioxide at any temperature and pressure (Figure 4). At high temperatures a large supply of carbon dioxide is required to satisfy calcite saturation because equilibrium carbon dioxide partial pressures are high at these high temperatures.

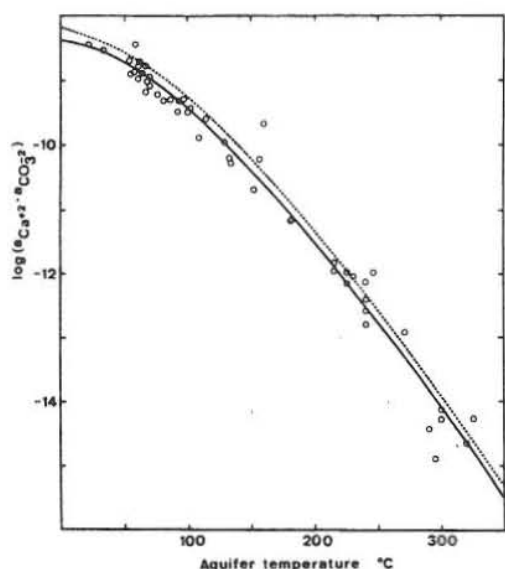


FIGURE 2: The state of calcite (solid line) and aragonite (broken line) saturation in selected Icelandic geothermal well waters (Arnorsson, 1989)

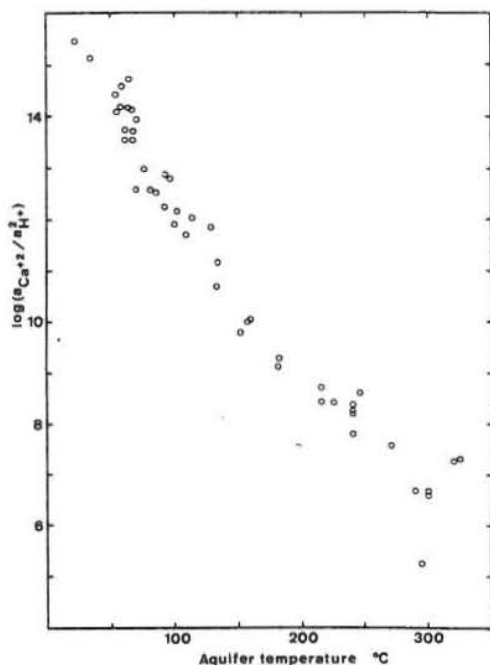


FIGURE 3: The ratios of calcium ion activity and the hydrogen ion activity squared at different temperatures in selected Icelandic geothermal well waters (Arnorsson, 1989)

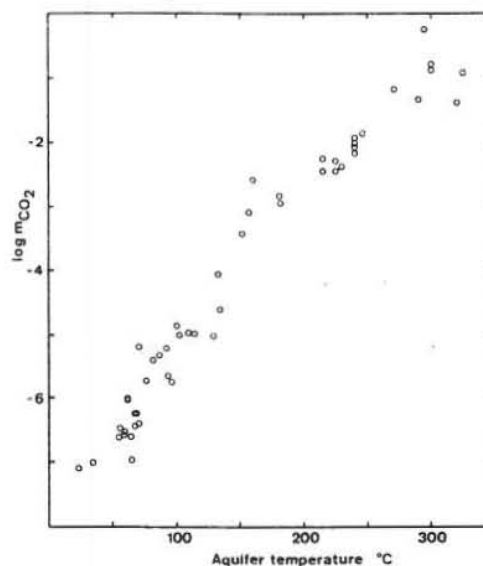


FIGURE 4: Carbon dioxide concentrations (moles/kg) in selected Icelandic geothermal well waters (Arnorsson, 1989)

Arnorsson (1978) has described in detail the changes that accompany the boiling of geothermal waters with respect to the state of calcite saturation. The degassing of carbon dioxide 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 an initially calcite saturated geothermal water supersaturated through boiling. If boiling is adiabatic the degree of supersaturation usually reaches maximum after cooling by some 10-40°C. The magnitude of supersaturation depends only on the extent to which the water is degassed. When saturation is at maximum the boiled water has been almost quantitatively degassed with respect to carbon dioxide. Further boiling which leads to the cooling of the water will cause successively decreasing supersaturation because the solubility of calcite increases with decreasing temperature.

2.3 Chemistry of calcite deposition

The solubility of carbonate minerals is strongly influenced by the pH and the activity of the carbon dioxide dissolved in geothermal waters. At any given

temperature, the solubility of calcite in solutions in equilibrium with a vapor phase increases with increasing carbon dioxide concentration up to about 1 mole carbon dioxide per kg (Miller, 1952). In solutions held at a constant total pressure, the solubility increases with increasing carbon dioxide concentration up to about 1 mole/kg and then decreases toward higher carbon dioxide

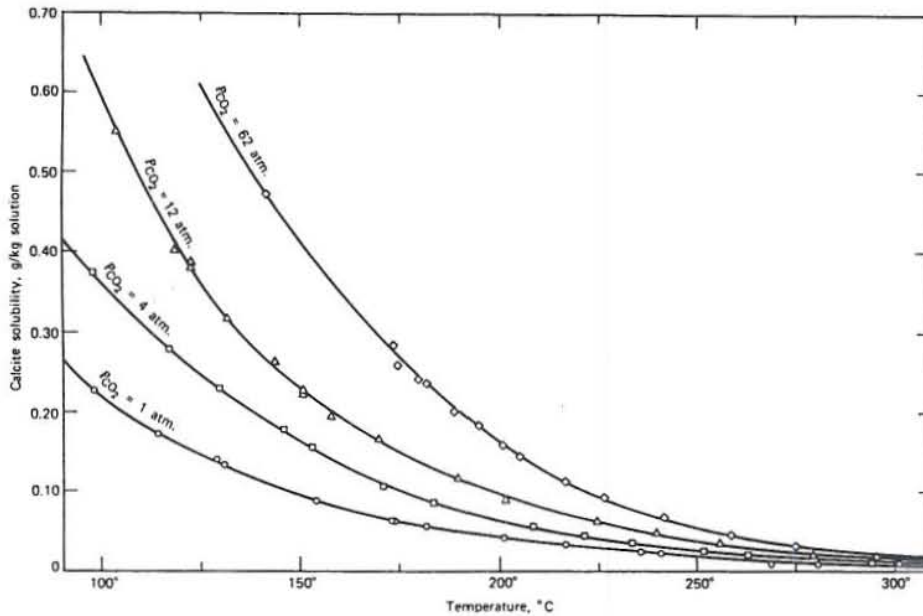


FIGURE 5: The solubility of calcite in water (Ellis, 1959)

concentrations (Sharp and Kennedy, 1965). At any given carbon dioxide pressure in the vapor phase, the solubility of calcite decreases with increasing temperature as shown in Figure 5 (Ellis, 1959).

Figure 6 shows the solubility surface of calcite in the system calcium carbonate - carbon dioxide - water, at temperatures up to 300°C and carbon dioxide pressures up to 70 atm (Sharp and Kennedy, 1965). Calcite can be deposited from solutions within the confines of Figure 6 by a decrease in total pressure at constant concentration of carbon dioxide and by a decrease in carbon dioxide concentration, due to boiling.

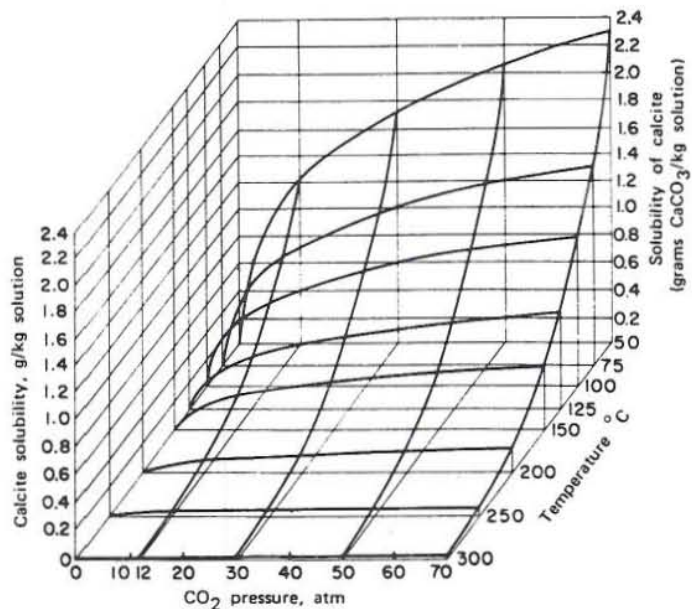


FIGURE 6: The solubility of calcite in the system calcium carbonate - carbon dioxide - water (Sharp and Kennedy, 1965)

Calcium carbonate precipitates can form in geothermal waters by the combination of calcium ions with carbonate ions. The calcite scales form very rapidly once the thermodynamic conditions are correct. For practical purposes the calcite kinetics can be assumed to be instantaneous. The loss of carbon dioxide and the associated pH increase are the principal causes for calcite precipitation. Calcite solubility decreases as the temperature increases from 25 to 100°C and the solubility product continues to decrease up to 250°C (Figure 7). However, the presence of carbon dioxide at moderate to high pressure in a geothermal reservoir enhances its solubility. This dissolution reaction may be expressed as:

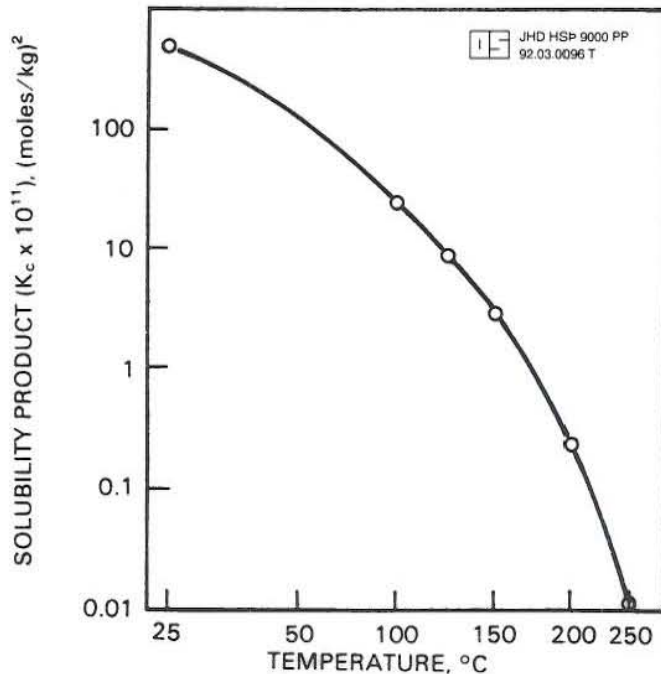
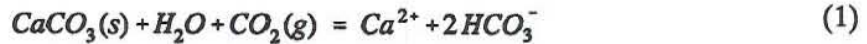


FIGURE 7: Solubility product of calcite as a function of temperature in water

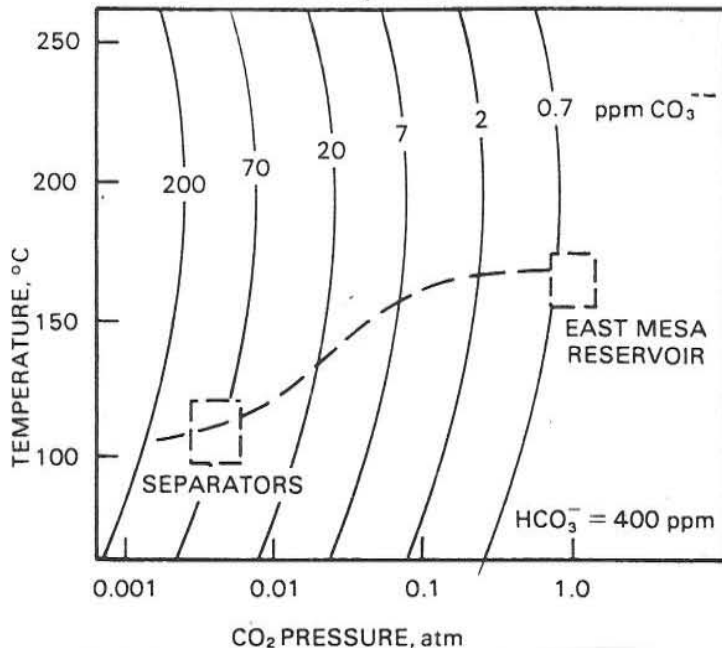
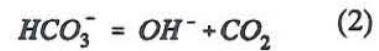
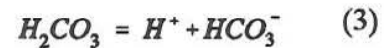


FIGURE 8: Isopleths showing carbonate ion concentrations versus temperature and carbon dioxide pressure (Michels, 1979)

As the bicarbonate ion dissociates to form the carbonate ion, the pH rises:



But in the equation the equilibrium is shifted to the left by the influence of increasing carbon dioxide pressure, which decreases the pH :



The carbonate concentration, which controls the solubility of calcite is shown in Figure 8 as a function of temperature and carbon dioxide pressure.

2.4 Calcite deposition

The three major classes of geothermal scales are generally considered to be

- silica and silicates;
- carbonate of calcium and iron;
- sulphides of iron and heavy metals.

Almost all geothermal systems contain dissolved carbon dioxide. According to Henry's law the amount of carbon dioxide present in a water at equilibrium is proportional to the pressure of the carbon dioxide in contact with the solution.

When geothermal waters are discharged from springs or geothermal wells, chemical reactions and evaporation occur with changes in temperature and pressure, and suspended materials are formed by chemical reactions and

microorganism activity. At the time of discharge, a geothermal water is saturated with chemical components due to degassing, concentration may take place by evaporation and chemical reactions, and finally material is removed from the geothermal water by deposition.

A small change in the concentration of a component can translate into a sizeable deposition rate in a geothermal well of high output. For example, a loss of 1 ppm of calcite from solution in a 20 cm diameter well producing 100 tons of water per hour, would give a deposit about 2 mm thick per day over 1 m length of pipe. Practically, deposition rates can be much greater than this. In severe scaling situations complete plugging of wells has occurred in a matter of days (Shimada, 1987).

The main factors affecting the formation of calcite are pH , pressure, temperature and salt concentration. At constant concentrations (of carbon dioxide and other constituents) calcite can not be deposited from geothermal water upon simple conductive cooling. On the other hand, the solubility is proportional to the carbon dioxide concentration (partial pressure).

Upon degassing the solubility of calcite decreases due to the reduction of partial pressure. Therefore, it is reasonable to consider that calcite tends to be deposited from water discharging from a reservoir with a high partial pressure of carbon dioxide because of its high solubility in reservoir water. In geothermal wells the usual mechanism of calcite precipitation involves the loss of carbon dioxide from solution and actually the tendency to form calcite deposits is greatest in geothermal fields with high carbon dioxide (bicarbonate) concentration (Shimada, 1987).

Pressure changes also influence the scaling potential of geothermal water. Large pressure changes occur during production from deep wells, and result in decreased pressures as the fluids are brought to the surface and used or processed. The partial pressure of carbon dioxide in the fluids from many of these wells is high. When waters are brought to the surface from these depths, drastic changes take place in the solubility properties of the water due to enormous decreases in pressure and temperature. Sometimes, even minor changes in pressure can alter the dissolution capacity of water. When rapid changes in conditions reduce the solubilities of the soluble constituents of the water, scale deposits form (Cowan and Weintritt, 1976).

The most important facts regarding calcium carbonate deposition problems are:

- 1) Deposits of it can be readily dissolved, transported or redeposited in water.
- 2) Carbon dioxide and water play major roles in its dissolution, transport and redeposition cycle.
- 3) Calcium carbonate scales are the most common of all geothermal scale deposits.
- 4) Calcium carbonate scale deposits can be prevented by pH adjustment or pressure adjustment.

Deposits of calcium carbonate can be readily dissolved and precipitated by water in a variety of conditions. Simple contact of water with air will expose the calcium to varying concentrations of carbon dioxide. The result of this combination is a potential precipitate that can adhere to surfaces and form a scale at some point in the water cycle (Cowan and Weintritt, 1976).

Calcium, bicarbonate and iron ions are common constituents of geothermal waters. These ions can form relatively insoluble carbonates through the loss of carbon dioxide. Deposition of calcium and iron carbonates can also be caused by electrochemical corrosion. Hydroxyl ions concentrated in cathodic areas of electrolytic cells in the screen and casing increase the precipitation of calcite which spreads to adjacent areas. The relation of corrosion to scaling is indicated by the fact that moderately corrosive waters saturated with calcite are known to have scaled steel well parts, whereas similar deposition did not occur when non-corrodable plastic filter pipes were used (Clarke and Barnes, 1969).

2.5 Prediction of calcite scale

Usually geothermal systems in which calcium carbonate scales tend to form have the following characteristics: their waters are of the bicarbonate type and weakly alkaline. If such geothermal fields are to be developed the calcite scaling potential has to be estimated.

Generally, the deposition potential can be estimated from the concentration of chemical components involved in deposition from the water, i.e., when the concentration is higher than the soluble concentration of the chemical compound, precipitation (deposition) of the chemical compound will occur in the water. At present, there are two methods to predict calcite scale formation from the chemical components of the water.

- 1) Saturation index (activity product).
This method involves the comparison of the calcium and carbonate ion activity product to the thermodynamic activity product. An expression of this, the saturation index, is sometimes used to predict scale formation:

$$SI = \log(Q/K) \quad (4)$$

If SI is higher than 0 a water can deposit calcite; if $SI = 0$ solubility exists; and if SI is lower than 0, a water does not have a calcite deposition potential (water is aggressive).

- 2) Langelier saturation index.
This is a method to predict scale formation by comparing the measured pH of a discharged geothermal water with the calculated pH of a water equilibrated with calcium carbonate, taking into account calcium ion concentration, alkalinity, temperature and total dissolved solids:

$$LSI = pH - pH_s \quad (5)$$

For an accurate application of these methods to geothermal waters, the chemical characteristics of the deep water have to be known. This can present problems.

The two methods described above should be used for qualitative predictions, because scale formation in wells and water-bearing rocks is difficult to predict quantitatively from chemical data on surface discharged water (Shimada, 1987).

Many different methods have been used to predict scale deposit formation. Some are theoretical and based on predicting precipitation, assuming that scale deposition will follow; others are empirical and based on observations on the behaviour of specific systems, where scale deposition is a problem. Both approaches have been applied in predicting the deposition of calcite. Despite the fact that many prognostic techniques are based on precise equations that predict precipitation, they all depend on the analysis of water samples collected in the field. Thus, in spite of their widespread use the prognostic methods can only indicate what might happen.

The problem of predicting scale formation is quite complex. For example, the same waters can form deposits in one section of a system and cause corrosion problems in another. Where a potential scale problem exists it is obviously desirable to be able to predict its extent. Analysis of produced waters may tell us what can be expected throughout the rest of the system. There are several mathematical approaches available for predicting the scaling tendencies of geothermal water. One of these is the WATCH aqueous speciation programme (Arnorsson et al., 1982).

2.6. Iron compound deposits

In natural waters iron occurs in two different states, ferrous and ferric iron. Thus, the chemistry of iron compounds in water is more complex than that of calcium carbonate scaling. Under certain conditions iron can precipitate to form scale deposits. One of the more common forms of iron scale is the oxide. Underground waters containing soluble iron oxidize readily once in contact with air in surface equipment. The product is a colloidal form of ferric oxide.

As geothermal waters, that discharge from formations containing large amounts of hydrogen sulphide, come into contact with iron, corrosion takes place and various forms of complex iron sulphides form. Most of them are insoluble and will form iron sulphide scales, e.g. pyrite or pyrrhotite, the form of which depends on the particular environment. The solubility of iron in oxidizing environments at pH levels near or slightly above neutral is sparse. Slight changes in pH or redox potential can be important in determining which compounds remain in solution and which are deposited. Iron may also be present in solution as a product of corrosion by carbon dioxide or hydrogen sulphide in geothermal waters. Precipitation of iron compounds is a particularly troublesome problem in injection wells and precautions aimed at maintaining oxygen-free systems together with the use of iron-sequestering agents are common deposit prevention techniques.

The chemistry of iron deposit formation is quite complex and its occurrence is relatively unpredictable (Cowan and Weintritt, 1976). Prognostic techniques offer general guidelines for predicting deposition. Yet it must be emphasized that all known prognostic methods are extremely limited and usually provide qualitative guidelines only.

2.7 Prevention of calcite scaling

Effective scale prevention in geothermal operations is often critical to the success of a project. Unfortunately, scale prevention methods must be designed to the very site-specific conditions in the field. These conditions dictate the type of scale prevention method that will be feasible.

Calcium carbonate scaling may be prevented by

- a) acting on carbon dioxide partial pressure;
- b) acting on the pH of the solution and;
- c) using chemical additives (scale inhibitors).

Pressure and temperature manipulations of the geothermal fluid can be achieved quite easily by pumping a geothermal well instead of relying on its natural flow. Utilizing a down-hole pump will drastically decrease or eliminate the in-hole pressure and temperature drops caused by flashing. The produced fluids can be maintained as a single phase system by means of a mechanical downhole pump. Thus, the formation of "pressure sensitive" scaling such as calcite can be eliminated. Another potential scale prevention method entails artificially maintaining a high carbon dioxide partial pressure by reinjecting some of the produced carbon dioxide back into the producing well, but it appears to work only for fluids with low carbon dioxide partial pressures.

Manipulation of the chemical composition of the geothermal fluid, particularly its pH , is another potentially valuable way to avoid scaling. Adding HCl to the geothermal fluid in order to decrease the pH below a certain value at which no calcite scaling can form is technically possible but expensive.

The utilization of scale inhibitors is the most common and promising method of combatting scaling problems. The main problem is to select the most suitable inhibitor among the hundreds of different chemicals on the market.

3. CORROSION

3.1 General

The word corrosion means the destruction of a material by chemical or electrochemical action of the surrounding environment. It is well known that iron and ordinary unalloyed steels corrode easily into rust. The most common case of corrosion is wet corrosion. The corrosive processes are very complex and take place in widely differing conditions (Hayashi, 1988).

The corrosive effects of a geothermal fluid on metals depend upon the chemical composition of that fluid. Geothermal waters have a wide range in composition, from strongly acidic waters containing sulfur and halogen acids which actively corrode most common alloys, to the more usual neutral-*pH* or slightly alkaline-*pH* waters, which may lay down protective scales of calcite, silica or metal oxides.

Contamination of geothermal fluids with oxygen (by aeration) drastically accelerates the surface corrosion of most alloys (Janik, 1985). Produced geothermal waters, not free of oxygen, may have been changed so as to lose dissolved gases, lose precipitated minerals or add atmospheric gases. The loss of dissolved gases is usually beneficial from a corrosion standpoint since the loss of carbon dioxide will tend to raise the *pH* in many geothermal waters. Corrosive attack on steel is reduced as the *pH* rises. Atmospheric gases can dissolve in the geothermal water if it is exposed to the atmosphere. The only gas of any corrosive consequence is oxygen. Although the solubility of oxygen decreases to a minimum as the temperature rises near 100°C, it is very important to exclude oxygen contact with geothermal water (Kindle et al., 1984).

Physical and biological factors help determine whether metal loss, mineral deposition or both will take place. Temperature can have a considerable effect on corrosion rates. If the *pH* is low and corrosion is controlled by hydrogen evolution, the metal loss will increase sharply with an increase in temperature. High pressure in a geothermal system favours high carbon dioxide content, low *pH* and acid corrosion, whereas reduction in pressure may result in the deposition of carbonates of calcium and iron and some protection film. A variety of bacteria that derive energy from the conversion of ferrous ion to insoluble ferric compounds can foul metal surfaces and promote pitting.

Most geothermal waters are at least mildly corrosive to iron but some will severely attack it and even affect more resistant metals. Water is likely to undergo change in chemical equilibrium when it is released or withdrawn from depth, and this may result in mineral deposition.

It is obvious that the many factors which influence corrosion and deposition cannot be considered one at a time when predicting the ultimate effect. Numerous investigators have attempted to integrate them into meaningful indices: e.g. the carbonate saturation index of Langelier and the stability index of Ryznar. Careful measurement of water quality parameters and systematic analysis of the data allow one to predict potential problems and to plan accordingly. For those problems which cannot be easily anticipated or avoided, there are effective diagnostic tools and corrective measures.

3.2 Types of corrosion

This part of the report is based on the papers of Corsi (1986), De Berry et al. (1978) and Hayashi (1988). Generally speaking, we can find all the different types of corrosion in geothermal equipment and it appears useful to recall the main characteristics of each.

Uniform or general corrosion is a general all-over attack on the metal surface that is transformed into rust. Uniform corrosion is often promoted by chloride or hydrogen ions. This type of corrosion is not of great concern because the lifetime of equipment can be accurately estimated on the basis of simple tests.

Pitting is a localized form of attack in which pits develop in the metal surface. Pitting is often associated with the breakdown of a passivation film or surface scale. High concentrations of chloride and hydrogen ions stimulate the dissolution of most metals. For the initiation of the pitting corrosion the rate of metal dissolution needs to be momentarily high at one particular point. Among the many factors that affect resistance to pitting, the following shall be discussed in greater detail. The only thing that can be said in general for all stainless steels is that the region *pH* above 12 is relatively riskfree. Laboratory experiments with conventional 18/8 steel have shown that a 4 % *NaCl* solution provides the most frequent and deepest pits at *pH* between 4 and 8. The cathodic reaction occurring in conjunction with this pitting is considered to be the reduction of oxygen to hydroxyl ions. This means that the presence of oxygen is one absolute condition for the initiation of pitting. Oxygen, which has passivating properties against general corrosion, can thus be the direct cause of damage in an environment containing chloride ions. On the other hand, the attack is rapidly accelerated if oxygen is present, since it acts as a cathodic depolarizer. Pitting, just as all electrochemical corrosion, is hastened by elevated temperatures. However at atmospheric pressure a temperature rise to above about 80°C can have a secondary effect involving a reduction in the intensity of pitting due to the fact that the content of dissolved oxygen is reduced because of its reduced solubility. Note, however, that this does not apply in systems kept under pressure.

Crevice corrosion is similar to pitting in that it is a localized attack. It occurs in crevices of equipment or under scale deposits. Contact between metal and nonmetal surfaces can cause crevice corrosion. Deposits such as corrosion products and scale deposits may produce crevice corrosion. As corrosion proceeds, oxygen within the crevice is consumed. Both chloride and hydrogen ions accelerate the dissolution of iron.

Stress corrosion cracking (SCC) is a type of failure promoted by a combination of the action of specific chemicals, such as chloride ion and tensile stress. The presence of oxygen and increased temperatures increase the severity of attack. This is the most dangerous form of corrosion in geothermal environments. The most common agents that cause stress corrosion cracking are hydrogen sulphide and chloride. Aqueous solutions containing large amounts of hydrogen sulphide cause a form of stress corrosion cracking in 18/8 steel at low *pH*, especially below *pH* 4. Stress corrosion cracking caused by hydrogen sulphide is transcrystalline. This form of corrosion takes place primarily at low temperatures. At higher temperatures the solubility of hydrogen sulphide in water decreases in open systems. Oddly enough, this susceptibility is also less in closed, pressurised systems at, for example, 120°C. One possible explanation is that protective sulphide films are formed on the steel surface.

Sulphide stress cracking is a form of corrosion that may occur due to tensile stress and environments involving hydrogen sulphide in an aqueous phase. Low *pH* greatly accelerates material failure. Hydrogen blistering which may occur in low strength steels exposed to waters containing hydrogen sulphide is similar. Sulphide stress cracking decreases in severity with increased temperature.

Other types of corrosion include galvanic corrosion, corrosion fatigue and exfoliation, which involves the formation of layers of corrosion products, but these are less important in geothermal system.

3.3 Key Species

Once the geothermal water is available for use, two important technological problems confront us; i.e. the prevention of scaling and corrosion. Silica and calcite and sometimes sulphide are the most important scales. Corrosion products are a second source of scale forming species. Both these sources of scales are important because of the adverse effect of scale on heat transfer and pumping efficiency (production or reinjection).

The species that are of greatest interest in geothermal water in relation to corrosion are hydrogen ion, chloride ion, hydrogen sulphide, carbon dioxide, oxygen and iron.

Hydrogen ion. The corrosion rate of most materials increases as the *pH* decreases. The susceptibility of steels to stress corrosion cracking increases with increasing hydrogen ion concentration (lower *pH*). The main types of corrosion are pitting, crevice and stress corrosion cracking. The *pH* is a particularly significant characteristic of well water. A value of 6.5 or below, in a water with a high carbon dioxide concentration (e.g. 20 mg/l) indicates that acid attack and direct hydrogen evolution are likely to occur, if the water is in contact with iron or steel. Higher *pH* values (above 8) are usually associated with waters that cause localized pitting instead of general corrosion, particularly if dissolved oxygen is present, and such waters may also scale well parts with carbonate deposits. Generally speaking, the lower the *pH*, the more corrosive the water is to iron well construction materials.

Chloride ion. This ion causes local breakdown of passive films. Uniform (general) corrosion can also increase with increased chloride ion concentration, but this action is generally less serious than local forms of attack. It is known that 5-10 ppm of chloride ion may be sufficient at temperatures higher than 50°C to promote stress corrosion cracking in stainless steel. A high chloride concentration causes increased solubility of iron in geothermal water by forming highly soluble complexes with the ferric ion.

Hydrogen sulphide. Probably the most severe effect of hydrogen sulphide is its attack on *Cu* and *Ni* alloys. The effect of hydrogen sulphide on iron compounds is less predictable. Accelerated attack occurs in some cases and inhibition in others. High-strength steels are often subject to sulphide stress cracking. Oxidation of hydrogen sulphide in aerated geothermal process streams increases the acidity of the stream. Hydrogen sulphide is ubiquitous at the parts per million or parts per billion levels in geothermal waters. A low concentration may have a serious detrimental effect especially if oxygen is also present. General corrosion by hydrogen sulphide in geothermal waters proceeds in such a way that iron is oxidized to soluble ferrous iron at the anode and hydrogen sulphide dissociates into hydrosulphide and sulphide ions at the cathode. The threshold concentration for attack is less than 30 ppb hydrogen sulphide. The presence of hydrogen sulphide in geothermal waters, like the presence of iron, indicates a reducing water capable of dissolving iron. In addition, it indicates the presence of a sufficient concentration of hydrogen sulphide to corrode iron and steel significantly through direct combination with the metal and development of secondary corrosion cells. When hydrogen sulphide in low temperature waters is detected there is a reason to suspect the presence of sulphate-reducing bacteria and these can cause troublesome and very persistent localized pitting in addition to the general sulphide attack. Hydrogen sulphide concentrations of 0.5 ppm or more can damage certain copper alloys.

Carbon dioxide. Carbon dioxide is a mild oxidizing agent that causes increased corrosion of steel. However, the primary effects of carbon dioxide in geothermal systems involve carbonate species and *pH* changes. In acidic solutions, carbon dioxide can accelerate the uniform corrosion of carbon steels. The *pH* of geothermal waters is largely controlled by carbon dioxide. On the other hand, bicarbonates and carbonates can display mild inhibitive effects. Carbon dioxide occurs

naturally in many geothermal waters and has a major corrosive effect on steels. Theoretical considerations show a very high uniform corrosion rate in the presence of carbon dioxide and sodium chloride up to about 80°C. At higher temperatures stable iron carbonate films, which slow the corrosion rate compared to predicted values, are formed. Carbonic acid itself is also believed to provide for an alternative cathodic half-reaction which yields bicarbonate ions and hydrogen.

Oxygen. Oxygen is present in low concentrations in most geothermal waters. On the other hand, the inadvertent intrusion of even traces of this gas into geothermal waters has led to greatly accelerated corrosion. The co-occurrence of oxygen and chloride can cause failure due to stress corrosion cracking. The addition of minor quantities of oxygen to a geothermal system can greatly increase the chance of severe localized corrosion of normally resistant metals. The corrosion of carbon steels is sensitive to trace amounts of oxygen. Despite low concentrations of hydrogen sulphide, dissolved oxygen from the air may persist in low temperature geothermal waters for some minutes, because of slow reaction kinetics. Preventing oxygen contamination is extremely difficult, especially if pumps other than downhole submersibles are used to move the geothermal water. The geothermal water may come into contact with the atmosphere (during reinjection) or oxygen might be one of the natural components in a gas accompanying the geothermal water. Aerated water causes a tenfold or greater increase in the uniform corrosion rate. Together with chloride ion, oxygen can initiate stress corrosion cracking at a certain temperature. It is very

important to avoid oxygen contamination in the reinjection lines at those points where the temperature may increase when the water flows into the injection wells. The corrosion of steel in aerated water is controlled by the reduction of dissolved oxygen on an iron-oxide covered surface and dissolution of iron under occlusions on the surface. Only a few ppb of oxygen in hot water are needed to cause localized corrosion and pitting. Figure 9 shows the effect of oxygen contamination on the corrosion rate of carbon steel in seawater at 120°C. It has been shown that oxygen can act either as a cathodic depolarizer or oxidize hydrogen sulphide to elemental sulphur or sulphuric acid in the presence of a catalyst (ferrous ion). Even small amounts of oxygen can cause extensive corrosion damage. At low oxygen levels, the corrosion products are mainly iron sulphides (pyrite, pyrrotite). As the oxygen level was increased magnetite became the major product.

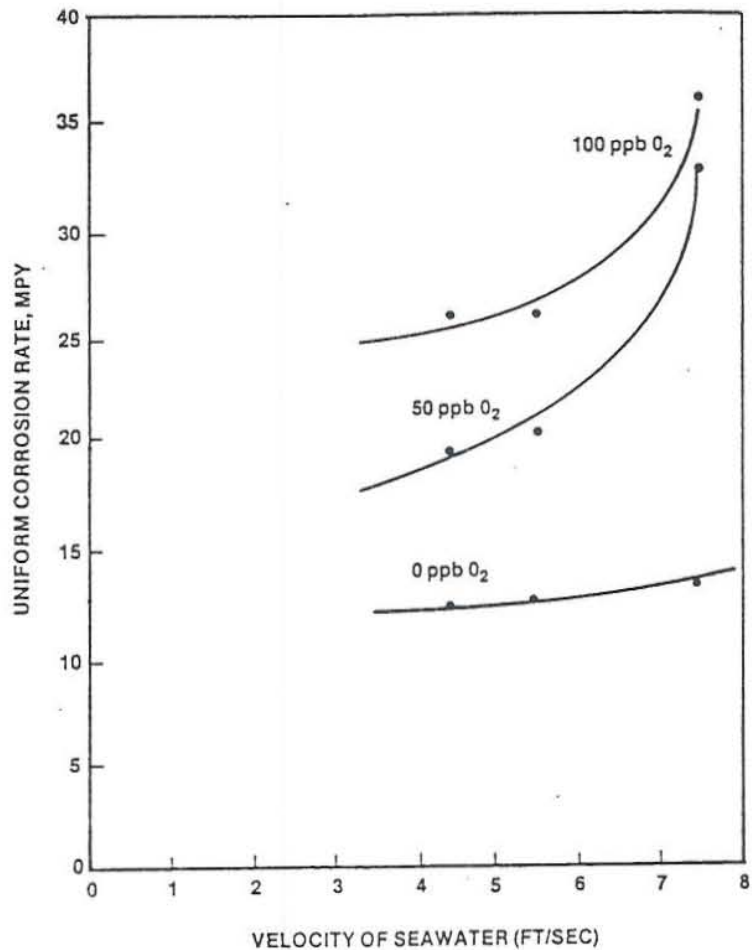


FIGURE 9: Effect of oxygen on uniform corrosion rate (George et al., 1975)

Dissolved iron. The presence of heavy reddish-brown iron oxide stains in well discharge indicates an anaerobic well water, i.e. a reducing environment, capable of dissolving iron from both the aquifer rock and the steel well parts. In addition to its power to corrode, such water may also cause troublesome iron deposits in any part of the system that is exposed to oxygen by aeration or mixing with water of different quality. When pH and redox potential, Eh , are plotted on an iron stability diagram, additional information concerning the water's capacity to corrode or protect iron surfaces is obtained. If the geothermal water parameters plot in the ferrous ion area of the diagram, the water can be expected to dissolve iron. If they plot in the ferric hydroxide area corrosion will be inhibited by oxidation products, and scaling may occur.

And finally a few words about **temperature**. An elevated temperature is most damaging to a well water of high carbon dioxide content and low pH . The hydrogen evolution reaction rate doubles for each $10^{\circ}C$ increase in temperature. A water of $35^{\circ}C$ will, therefore, be twice as destructive to steel as one at $25^{\circ}C$. At higher temperatures this effect can be extremely damaging.

TABLE 1: Principal effects of the main corrosive species

Species	Effects
oxygen	concentrations above 50 ppb cause pitting
pH	corrosion rate decreases above $pH=8$
carbon dioxide	lowers pH , increases corrosion
hydrogen sulphide	cathodic poison, promotes SSC
temperature	increase accelerates damage
chloride ion	promotes SCC and general corrosion

Scale deposition can influence the corrosion of metals. Calcium carbonate scale is sometimes deposited intentionally in order to provide protection against corrosion. More often, however, scale deposits accelerate corrosion rates. Iron sulphide scale deposits cause particularly severe problems. The iron sulphide is cathodic to iron, setting up a galvanic cell subsequently causing severe pitting. The presence of any type of deposit in waters containing gases (hydrogen sulphide, oxygen or carbon dioxide) will usually increase the severity of any potential corrosion problem.

Scaling or solids deposition is another aspect of geothermal fluid chemistry that influences materials performance. Precipitation of solid phase species from a solution or on equipment surfaces can influence corrosion rates and cause erosion. The composition of the solids formed by scaling and the rate of precipitation depend on the fluid composition and specific process stream conditions; therefore, solids formed by scaling are not included in the list of key corrosion species.

Generally, the aggressiveness of a particular species varies from one material to the next. Often the interaction of two or more species with specific materials has a different effect from that of each species on its own. Also, the temperature dependence of the corrosion of a given material by a given species is often undefined. Finally, the importance of a given species depends on the form of attack under consideration (Conover et al., 1980).

3.4 Prediction

As stated earlier the concentrations of chemical constituents in geothermal waters can be used to predict the kinds of problems which might be encountered. Corrosion and scaling processes are complex and interactive. For this reason, no single test or index is an infallible indicator of

these processes. Nevertheless, certain accelerated performance tests and indices already mentioned have proven to be of considerable value in selecting construction materials. If the geothermal water is saturated or supersaturated with respect to calcite, mineral scaling may occur along with moderate corrosion. Localized corrosion processes, such as that related to bacterial sulphate reduction, can cause severe damage to steel. The pH value can be used as a semiquantitative indicator of the probable intensity or corrosion attack, as well as an indicator of the water's tendency to cause scaling rather than corrosion. Waters with pH below 6.5 are likely to be severely or extremely corrosive to steel and moderately corrosive to alloys such as brass (yellow and red). Waters with pH above 7.5 are more likely to be moderately or mildly corrosive to steel. Scaling may occur at a higher pH , particularly on steel surfaces.

A water saturated with calcium carbonate tends to precipitate a scale that may protect against corrosion. The degree of calcite saturation is a useful index in corrosion and scaling studies. The Langelier saturation index is considered to be essentially a qualitative tool which may yield positive values even for corrosive waters. The stability index proposed by Ryznar is a more quantitative indicator. But it is unlikely that either of the indices takes into full account the localized effect of acidic carbon dioxide bubbles at points of pressure changes. Thus, a water of a high carbon dioxide concentration may be more destructive than conventional criteria indicate. There is a reason to suspect significant localized damage at least to iron and steel when the carbon dioxide concentration exceeds 20 mg/l regardless of the index value (Clarke, 1980). The Ryznar index and other indices based on calcite saturation should not be used to predict corrosion (no significant correlation is between corrosion and the Ryznar index) (Ellis, 1959).

Redox potential - pH diagrams, which summarize the thermodynamic properties of a system, are extensively used for interpreting the corrosion behaviour of metals in geothermal waters. Redox potentials are very useful in predicting corrosion behaviour. All metals with redox potentials more negative (active) than hydrogen will tend to be corroded by acid solutions. If dissolved oxygen is present, there is a possibility of oxygen reduction and corrosion. The application of thermodynamics to corrosion phenomena was generalized by M. Pourbaix with Eh/pH diagrams. The diagrams are constructed from calculations based on the Nernst equation and solubility data for various metal compounds (Hayashi, 1988). The relationship of oxidizing and reducing constituents determined by measuring the potential between a platinum and a reference electrode immersed in the water, can have a significant effect on the corrosiveness. This potential, which is called the redox potential or the Eh value, together with the corresponding pH value, indicates the ionic and molecular forms likely to be present in the particular water being tested, and thus, reveals whether metal dissolution or metal protection can be expected. For example, if the ferrous ion is the stable form, corrosion would be expected to proceed because this ion is soluble and a non-protective product of the anodic corrosion process. On the other hand, if semi-protective ferric hydroxide predominates, the water will be less aggressive to steel (Clarke, 1980). The Pourbaix diagram for iron is shown in Figure 10.

It is possible to delineate areas in which iron, iron-hydroxide, ferrous ions, etc., are thermodynamically stable. The Eh/pH diagrams represent equilibrium conditions and should never be used to predict the rate of a reaction. Although the spontaneous direction of a reaction may be in the direction of metal corrosion, this does not necessarily indicate that corrosion will take place. The rate of corrosion is another problem (Hayashi, 1988).

In the analysis of corrosion phenomena, it is necessary to have some knowledge of the equilibrium conditions in the system. Such information not only indicates whether or not any given process is spontaneous, but also defines the conditions that must be achieved in order to minimize the effects of corrosion in practical systems. An Eh/pH diagram is presented for iron in sulphide containing geothermal water at 25°C. The geothermal water contains 10 ppm of total dissolved sulphide (Figure 11).

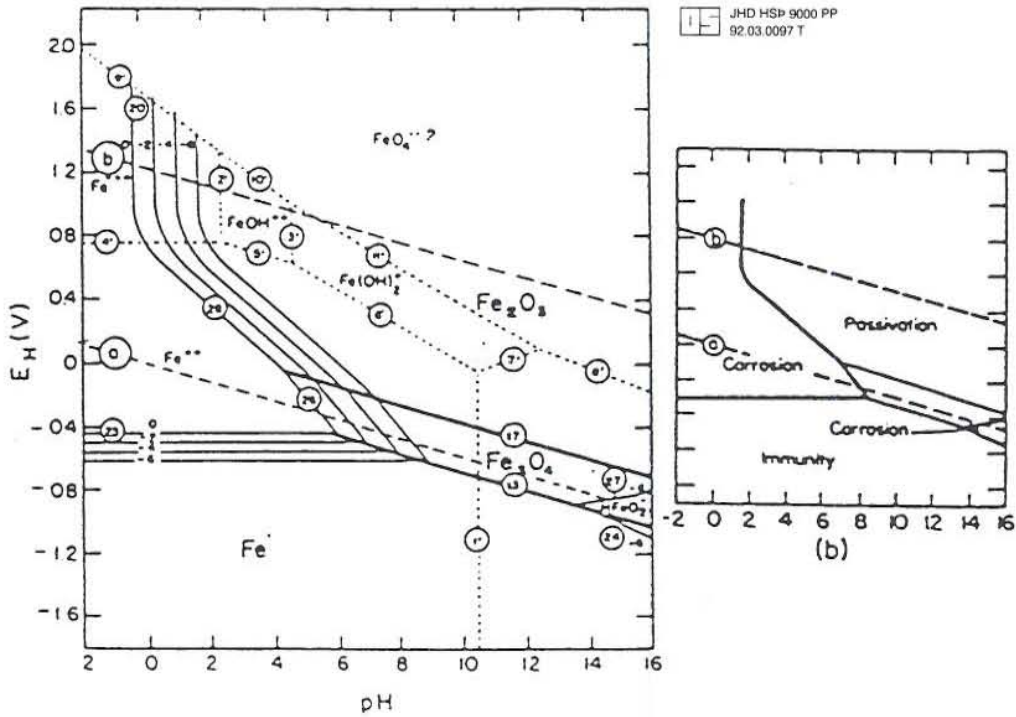
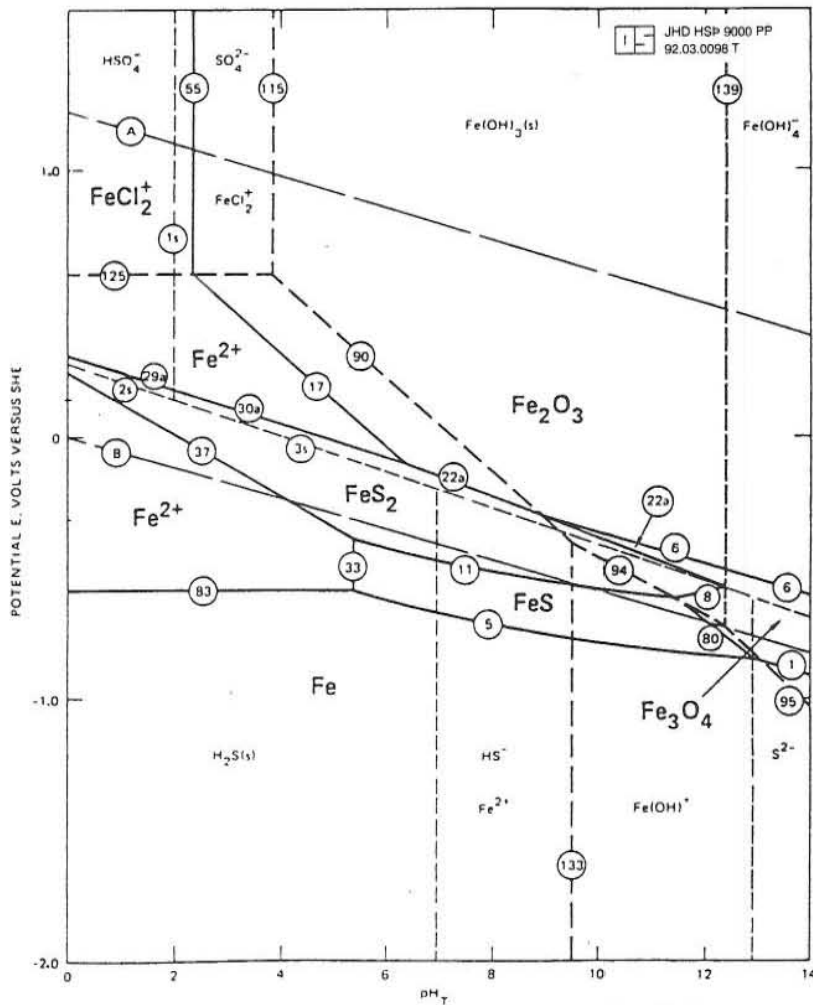


FIGURE 10: *Eh/pH* equilibrium diagram for the system iron-water



Eh/pH diagrams are principally useful as a didactic tool illustrating the relationship between *pH*, redox potential and other solution properties. Even when redox potential can be accurately determined, concepts of equilibrium thermodynamics can only be used to assess whether corrosion is likely or not.

FIGURE 11: *Eh/pH* diagram for iron in geothermal water at 25°C in the presence of 10 ppm total dissolved sulphide and activities of dissolved iron species 5.8 ppm

4. RESULTS AND CONCLUSIONS

4.1 Description of work

Data on the composition of geothermal waters from Serbia from Papic (1991) and Milivojevic (1989) have been used. Analyses were done by the author of this report as well as the Chemical Research Company "HIZIP", Belgrade. All analytical determinations were done by standard methods (Table 2). The results of the chemical analyses are shown in Tables 3 and 4.

TABLE 2: Analytical methods used in hydrochemical investigations in Serbia

Parameter	Analytical method
<i>pH</i>	pH-meter, combined electrode (HACH, USA)
<i>Eh</i>	SCE with <i>Pt</i> -electrode, <i>pH</i> -meter
<i>SiO₂</i>	yellow-silicomolybdenic acid, spectrophotometer
<i>Na</i>	atomic absorption spectrophotometer
<i>K</i>	atomic absorption spectrophotometer
<i>Ca</i>	atomic absorption spectrophotometer
<i>Mg</i>	atomic absorption spectrophotometer
<i>Fe</i>	o-phenantroline, spectrophotometer
total <i>CO₂</i>	titration with 0.01 M <i>HCl</i> , <i>pH</i> -meter
<i>SO₄</i>	turbidimeter (HACH, USA)
<i>H₂S</i>	titration with <i>Hg(CH₃COO)₂</i> using dithizone as indicator
<i>Cl</i>	Mohr titration and ion selective electrode (Radiometer)
<i>F</i>	ion selective electrode (Radiometer)

In the first part of the project which relates to the determination of scaling potential of selected geothermal waters in Serbia, the results of chemical analyses are interpreted using the WATCH programme. This interpretation can be summarized as follows:

1. Creating a WATCH 2 programme input data file assuming that no boiling has taken place before sampling, and running the programme for calculation. The computer output is used to construct curves for the temperature dependence of the calcite activity product, the carbon dioxide concentration and the ratio of the calcium ion activity to the hydrogen ion square activity.
2. Creating a WATCH 2 programme input data file for adiabatic boiling and running the programme for calculation. The ratios of the activity products to the solubility products of calcite are compared at different measured temperatures. The computer output is used to construct curves showing the temperature dependence of the saturation index. Curves showing the dependence of $\log Q$ on various degassing factors were created for seven selected geothermal waters in the temperature range 25 to 94°C.
3. Creating a WATCH 2 programme input data file for the heating of selected spent geothermal waters up to the measured temperatures in production aquifers, or up to the temperatures predicted with the chalcedony geothermometer and then creating the curves for the saturation index dependence on temperature. The last step is the quantification of calcite scale. The extent of scaling is estimated from amount of discharge, then multiplied by discharge measured in amount per time to obtain amount of scale per unit time.

TABLE 3: Chemical composition of selected geothermal waters in Serbia

No.	Locality	T °C	pH/T /°C	SiO ₂ mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	CO ₂ mg/l	SO ₄ mg/l	Cl mg/l	F mg/l
1	Svrackovci	28	9.48/22	33	35	0.3	4	1	50	6	7.1	2.5
2	Prolom spa	30	9.00/20	40	49.4	0.2	3.5	0.5	88	5	7.1	0.2
3	Josanicka spa	78	9.30/22	97	81	2	5.4	2.9	93	26	24	5.4
4	Slanaca	37	9.44/22	97	81	2	5.4	2.9	93	26	24	5.4
5	Ribarska spa	51	9.18/22	107	84.2	1.8	5.8	0.2	92	59	6.6	2.5
6	Brestovac	41	8.55/20	56	124	2	88	0.2	35	400	21	0.9
7	Bogatic	75	7.09/22	64	150	10.6	37	10.2	354	3	105	1.5
8	Smed. Palanka	48	7.2/22	37	200	107.3	10	19.6	3820	10.6	452.3	8.1
9	Selters	50	7.17/22	28.7	2100	43.8	13.2	20	2150	0.5	1971	2.7
10	Suva Cesma	22	6.66/22	106	958	34	10.6	27.4	2753	52.3	125	7
11	Vica	21.4	7.24/22	76.5	947	34	16.2	113.2	2400	3.1	123.4	15.6
12	Bukovicka spa	31	6.56/22	94.3	925	67	18.8	13	2538	1.7	24.1	4.6
13	Cibutkovicica	20.8	6.29/20	69	442	81.2	32.3	70.3	2798	2.9	22.53	0.8
14	Sierinska spa	68	7.17/22	137	1210	66.7	9.8	19.4	2852	44.4	99.9	2.5
15	Bujanovacka spa	45	6.65/20	130	1159	60	9	12.7	3186	90	61	6
16	Vrnjci	35	6.29/22	124	490	74.8	70.5	66.7	2910	2	42.5	2.4
17	Kursumlija	65	6.9/22	80	640	46	30	33	1670	20	35.5	3.7
18	Rajcinovici	35	6.6/20	59	572	236	65	15	2006	2	126	5.2
19	Rakovac	42	6.8/20	42	1443	47	40	21	3550	180	67	12
20	Pozarevac	36	8.2/20	42	345	1.6	3	1.8	500	3	128	0.52
21	Avala	26	8.5/20	22	50	3.4	20	27.2	193	18	35.5	0.30
22	Dublje	50	7.2/22	34	174	11.5	30	11	450	2.5	55	2.60
23	Ljig	32	7.6/22	25	261	8.5	22.4	21.8	600	2.2	37.6	2.2
24	Vrujci	26	7.46/22	17.3	16	1.7	39.3	17.9	178	0.9	14.2	0.4
25	G.Trepca	31	7.75/22	19	5.6	1.8	39.7	58.4	290	4.8	10.6	0.2
26	Mlakovac	28	7.5/22	24.6	24.7	5.7	57.9	44.6	348	17.5	16.5	0.60
27	Ovcara spa	39	7.2/22	22	20	3.5	98	40	380	18	14	0.8
28	Metkovic	55.4	7.09/20	31	268	16.8	27.9	8.5	611	1	141.8	2.40
29	Mataruska spa	43	7.5/20	70	2400	13.7	42	54.9	624.6	43	71	5.6
30	Bioska spa	36	7.4/20	7	2.8	0.5	47	18.3	160	8	14	0.1
31	Dag spa	30	7.5/20	9	3.2	0.8	64	18	218	6	7.1	0.1
32	Niska spa	34	7.2/20	24	22.7	1.2	62	14	164	40	28	0.4
33	Milkovac	30	7.3/20	11	5.7	0.8	78	15	251	6	7	0.1
34	Kravljansko Vrelo	32	7.2/20	22	7	1.6	66	23	250	14	10	0.2
35	Rgoste	30	7.4/20	16	6	1.2	82	20	273	14	7.1	0.1
36	Soko spa	43	7.2/22	24	7	8	74	17	225	20	14	0.2
37	Soko Banica	33	7.1/20	22	7	7.2	88	11	251	30	14	0.1
38	Nikolicevo	37	7.6/20	35	127	6.3	22	13.5	270	50	35.5	4.5
39	Sisevac	26	7.5/20	9	4.6	1.1	78	19	235	18	10	0.1
40	Despotovac	26	7.3/20	4	16.1	2	64	25.6	282	25	7.1	0.2
41	Cedovo	26	7.5/20	14	9	0.3	50	12	170	2	5	0.2
42	Vranska spa	94	7.4/22	129	266	13.8	20	3.4	324	235	46	8.2
43	Lukovska spa	63	6.7/22	50	255	19	105	18	793	117	85	2.0

In the second part of the project which relates to the assessment of the corrosion potential of selected geothermal waters in Serbia, the results of chemical analyses are interpreted using correlation diagrams for the main corrosion species in geothermal waters as well as *Eh/pH* diagrams. These correlation diagrams comprise redox potential, *pH* value, hydrogen sulphide concentration, oxygen concentration, carbon dioxide concentration and iron concentration.

TABLE 4: Key corrosive species in selected geothermal waters in Serbia

No.	Locality	Fe mg/l	CO ₂ mg/l	pH	O ₂ mg/l	H ₂ S mg/l	Eh mV	Cl mg/l
1	Bukovicka spa	2	1305	6.56	2.3	0.25	-56	21
2	Vrujci	0.1	18	7.46	6.6	.05	74	14
3	Svrackovci	0.09	0.06	9.48	1.1	0.65	-80	7
4	Mlakovac	0.05	32	7.5	5.6	0.01	140	17
5	G. Trepca	0.1	16	7.75	4.6	0.15	10	11
6	Ovcar spa	0.1	66	7.20	3	0.04	109	14
7	Bioska spa	0.12	24	7.40	5.3	0.12	64	14
8	Priboj spa	0.2	24	7.20	6	0.05	42	7
9	Mataruska spa	0.02	60	7.50	0.02	12.7	-310	71
10	Bogutovacka spa	0.025	34	7.10	0.05	3	-210	14
11	Rajcinovici	0.9	991	6.60	0.06	1	-150	126
12	Vranjska spa	0.04	80	7.4	0.50	0.34	-128	46
13	Rakovac	1	1222	6.8	2.05	0.34	0	67
14	Pazarska spa	0.02	176	6.8	0.02	4.8	-266	42
15	Banjof	0.8	530	6.4	3.3	0.2	16	14
16	Sijarinska spa	40	487	7.17	1.3	0.72	-108	100
17	Zvonacka spa	0.05	22	7.4	10.2	0.05	140	7
18	Dag spa	0.05	21	7.5	0.85	0.34	-107	7
19	Niska spa	0.08	30	7.2	0.45	0.4	-130	28
20	Prolom spa	0.2	0.36	9.0	1.05	0.68	-62	7
21	Kursumlija	0.7	410	6.9	0.22	0.77	-152	36
22	Lukovska spa	0.7	400	6.8	2.75	0.3	6	35
23	Ribarska spa	0.05	0.42	9.18	0.04	3	-208	6.6
24	Milkovac	0.1	37	7.3	1.10	0.25	-91	7
25	Kravljansko vrelo	0.1	45	7.2	3.55	0.25	47	10
26	Rgoste	0.2	75	7.4	2.15	0.17	11	7
27	Soko spa	0.14	40	7.2	1.35	0.6	-70	14
28	Soko banjica	0.1	55	7.1	1.7	0.25	-66	14
29	Josanica	0.2	70	7.3	2.35	0.34	1	7
30	Nikolicevo	0.15	22	7.6	1.70	0.34	22	36
31	Sarbanovac	0.01	0.2	8.5	3.30	0.25	12	14
32	Brestovac	0.025	0.5	8.55	0.45	0.34	-110	21
33	Vrnjci	1.4	2105	6.29	0.10	0.75	-184	43
34	Selters	0.52	351	7.17	0.15	1.44	-174	1971
35	Pozarevac	0.26	100	7.6	1.50	0.25	-26	128
36	Mionica	0.4	9	7.5	4.40	0.20	46	35
37	Suva Cesma	0.4	466	6.66	0.10	5.6	-210	128
38	Vica	0.4	400	7.24	1.85	0.34	36	142

4.2 Results and discussion

The main task of this project was to estimate the scaling and corrosion potential of selected geothermal waters in Serbia. At the beginning, a few words about chemical composition of geothermal waters in Serbia are needed. In Table 5 the average chemical composition of 43 selected geothermal waters is presented.

TABLE 5: The average chemical composition of selected geothermal waters in Serbia

Chemical component	Average value	Range
<i>pH</i>	7.5	6.29-9.48
CO_2 (mg/l)	200	0.2-2100
Na^+ (mg/l)	366	2.8-2100
HCO_3^- (mg/l)	1068	60-4700
Ca^{2+} (mg/l)	39	3-105
Cl^- (mg/l)	51	5-1971
Mg^{2+} (mg/l)	22	0.1-113.2
SO_4^{2-} (mg/l)	36	0.9-400
TDS (mg/l)	1254	138-10120
$\log Q/K$ - calcite	+0.175	-0.678 - +0.681

TABLE 6: Saturation indices for selected geothermal waters in Serbia

No.	Locality	T_m (°C)	$\log Q/K$	T_{chal} (°C)	$\log Q/K$
1	Vrujci	26	-0.08	35	-0.05
2	Vrnjci	35	+0.06	50	+0.10
3	Soko Spa	43	+0.04	60	+0.07
4	Metkovic	55	+0.11	60	+0.14
5	Lukovska Spa	63	+0.17	100	+0.35
6	Bogatic	75	+0.14	100	+0.25
7	Vranjska Spa	94	+0.27	125	+0.42

Table 6 shows saturation indices for selected samples. Generally, geothermal waters are supersaturated with respect to calcite as shown in Figures 12 and 13. However, some geothermal waters are undersaturated, mainly carbon dioxide-rich waters with *pH* values as low as 6.29.

The species which are most important from the point of view of calcite scaling, are *pH*, carbon dioxide and calcium ion. From Table 5 it can be seen that these geothermal waters are generally weakly basic, with a significant concentration of calcium ion as well as dissolved carbon dioxide and thus have a calcite scaling potential. The average value of the saturation index is +0.175, which makes these waters slightly supersaturated with respect to calcite. The ratio of the calcium ion activity to the square of the hydrogen ion activity is presented in Figure 14. On this figure we can differentiate three relations which illustrate the unequal variations of this parameter with temperature. The line at the top of the diagram relates to geothermal waters with *pH* above 8.5 and the bottom line to waters which are carbon dioxide-rich, i.e. with concentrations that exceed 100 mg/l. In the latter an increase is observed with increased temperature.

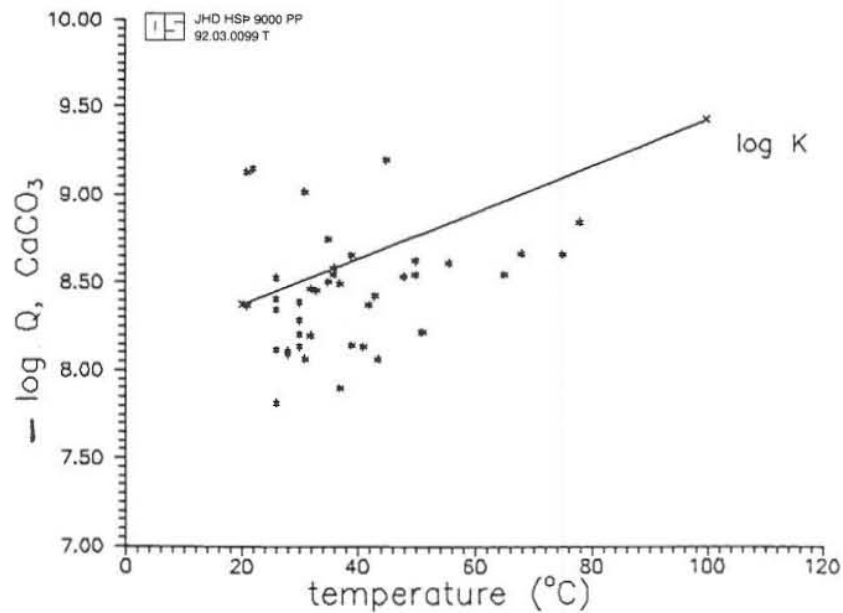


FIGURE 12: The state of calcite saturation in selected geothermal waters in Serbia

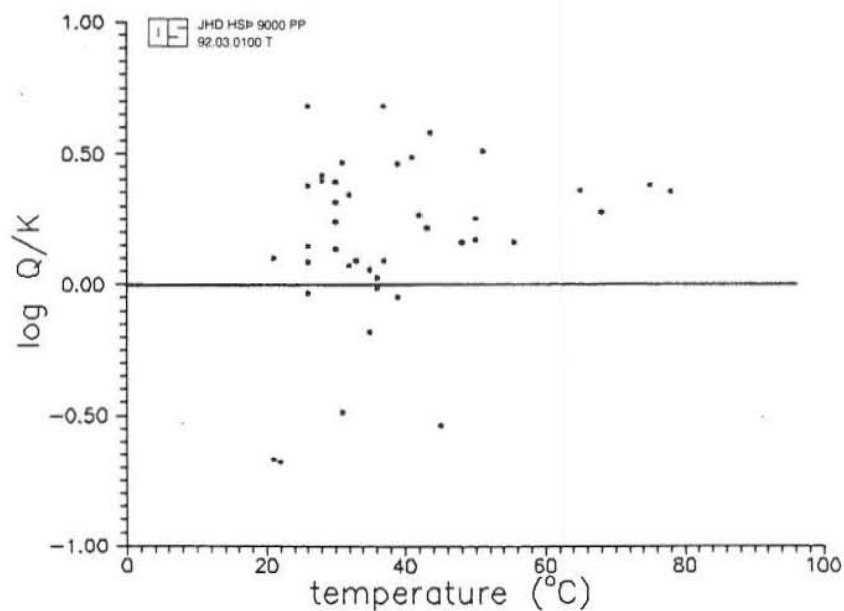


FIGURE 13: Saturation index of calcite in selected geothermal waters in Serbia

Similar trends are observed for carbon dioxide concentrations at different temperatures shown in Figure 15. The line for carbon dioxide-rich waters is presented at the top of the diagram, while at the bottom there is a line representing geothermal waters with pH above 8.5. These results are in agreement with results of Arnorsson (1989). However, we must keep in mind that these waters are from low temperature geothermal systems and that their dissolved carbon dioxide concentrations are significant.

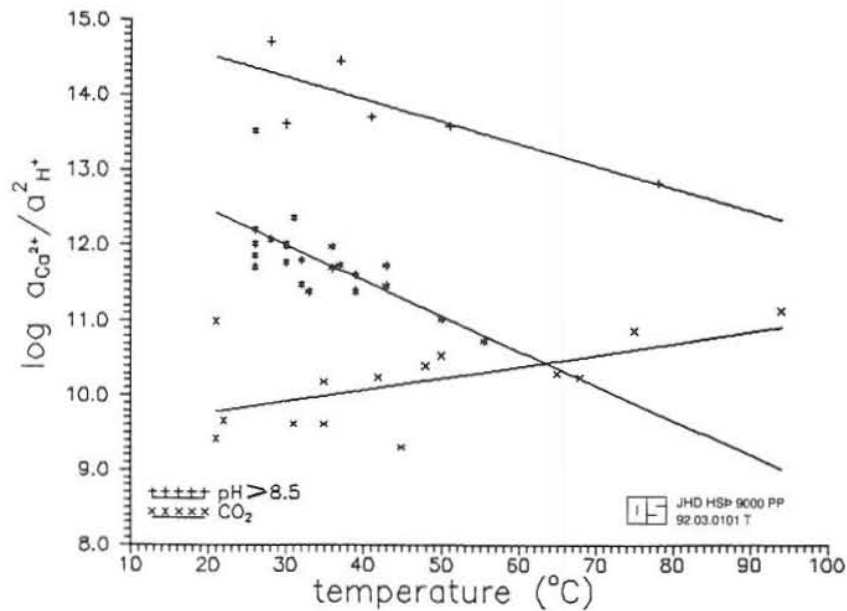


FIGURE 14: $Ca^{2+}/(H^+)^2$ activity ratios in selected geothermal waters in Serbia

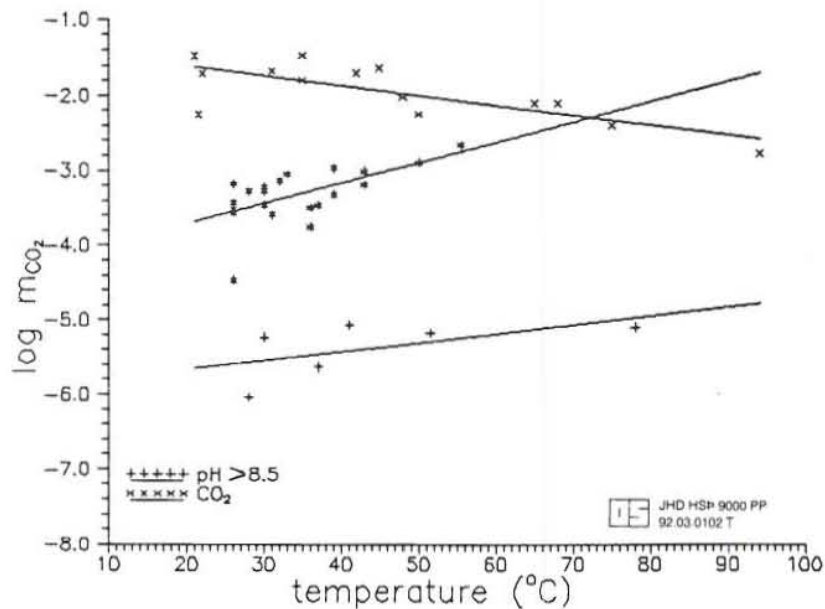


FIGURE 15: CO_2 concentrations (moles/kg) in selected geothermal waters in Serbia

It is known that with decreased temperature calcite becomes more soluble. When a geothermal well is discharged and the temperature is lowered there should be no calcite deposition problems. This is the case when the water is conductively cooled without steam formation. When flashing takes place, carbon dioxide is concentrated into steam, lowering the solubility of calcite in the remaining liquid.

The next step was the adiabatic boiling of geothermal waters down to 25°C, assuming that the degassing factor is small (AKF=0.01). Figure 16 shows the variation of the saturation index of geothermal waters with measured temperature. The lower curve represents geothermal waters

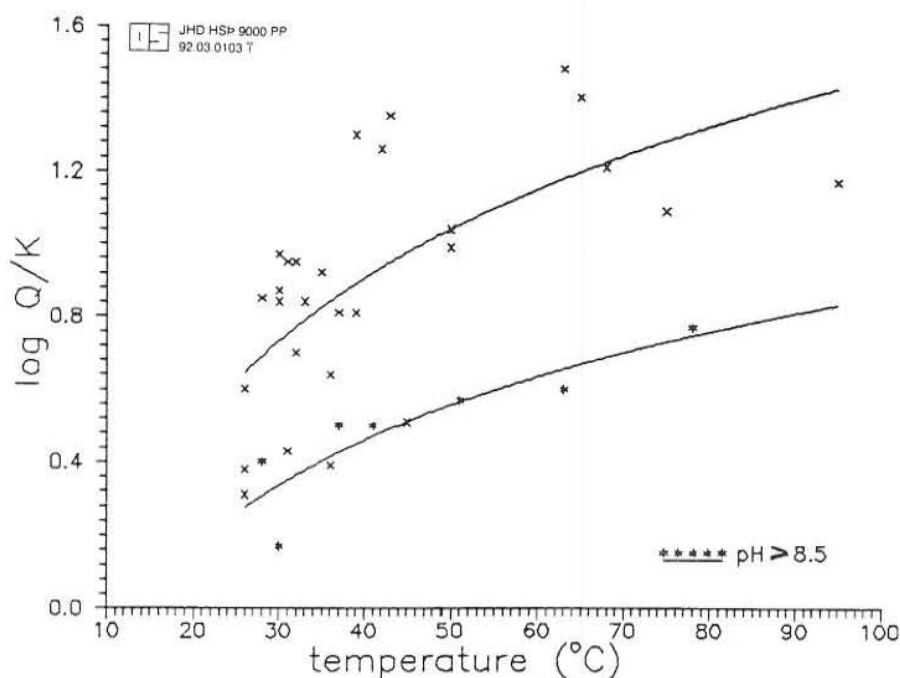


FIGURE 16: Saturation index of selected geothermal waters in Serbia (adiabatic boiling at 25°C ; $\text{AKF} = 0.01$)

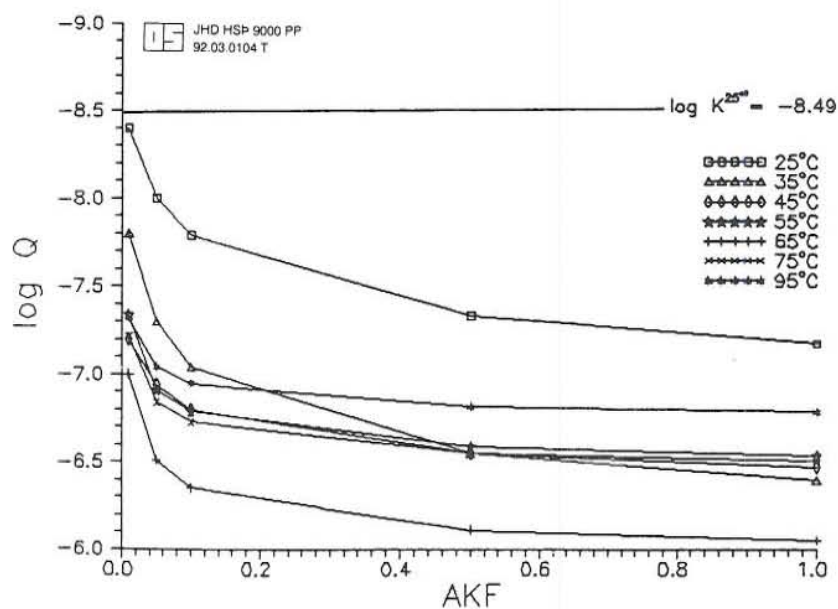


FIGURE 17: The state of calcite saturation for various degassing factors

with pH above 8.5. As can be seen from Figure 16 the values of the saturation index for these waters are in the range 0.2 to 0.75. For the other waters the values range from 0.3 to 1.5. Using higher degassing factors these values also become higher. So during this step geothermal waters became supersaturated to a great extent. The average value of the saturation index for selected geothermal waters is 0.828.

Figure 17 shows the changes in the saturation index for selected geothermal waters, at temperatures from 25 to 94°C , with different degassing factors (from 0.01 to 1.0).

In real situations water can be expected to be close to equilibrium with calcite, due to the fast rate of calcite deposition. Therefore a certain amount of calcium ion as well as the equivalent amount of total carbon dioxide has been subtracted. In this way, equilibrated spent geothermal water has been heated either up to the measured discharge temperature in the production well or up to the temperature predicted using the chalcedony geothermometer by simulation with the aid of the WATCH programme. The results for saturation indices for both cases are presented in Figures 18 and 19.

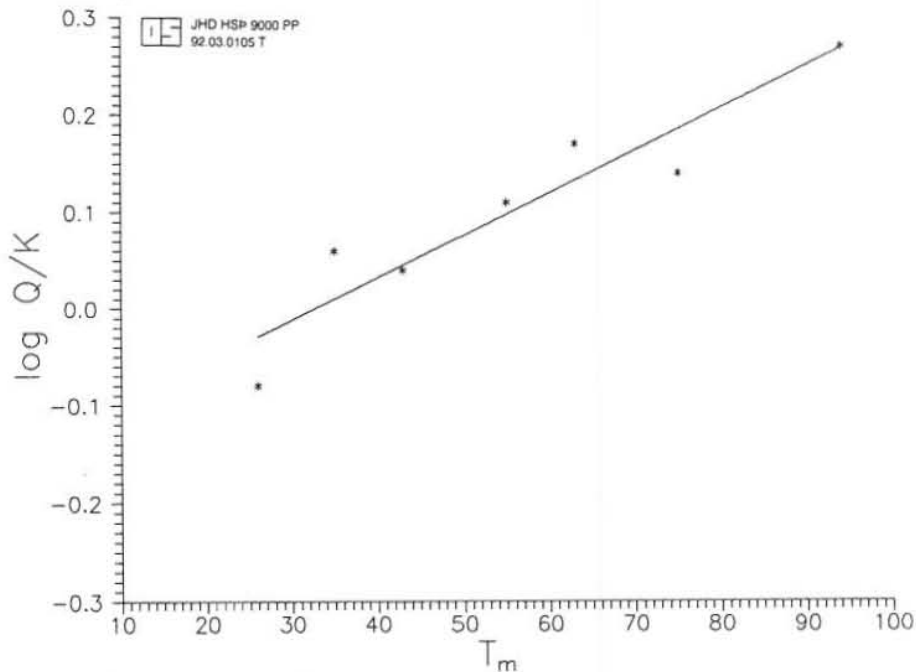


FIGURE 18: Saturation index after heating up to measured well temperature

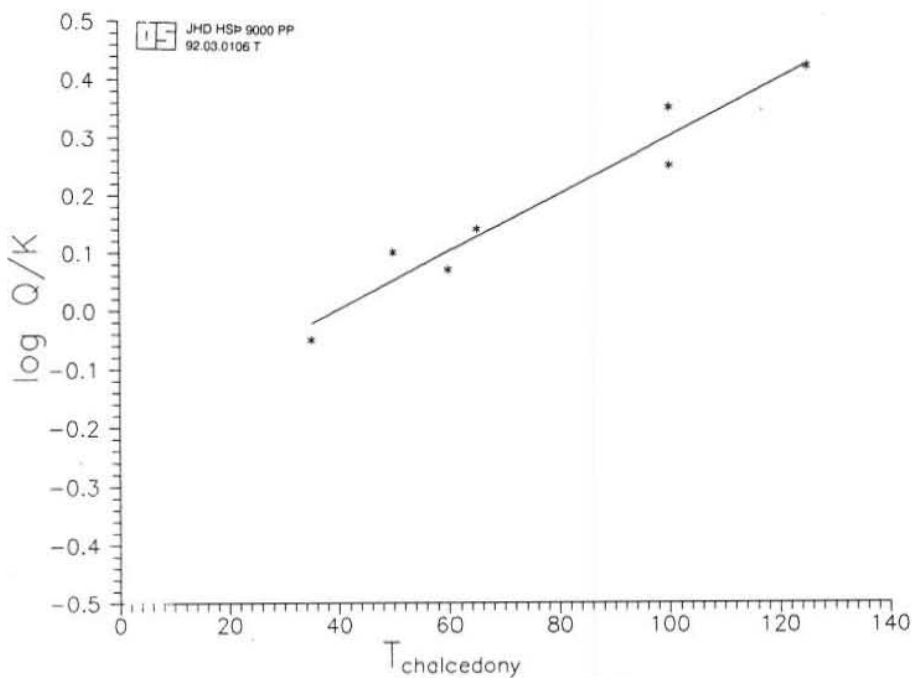


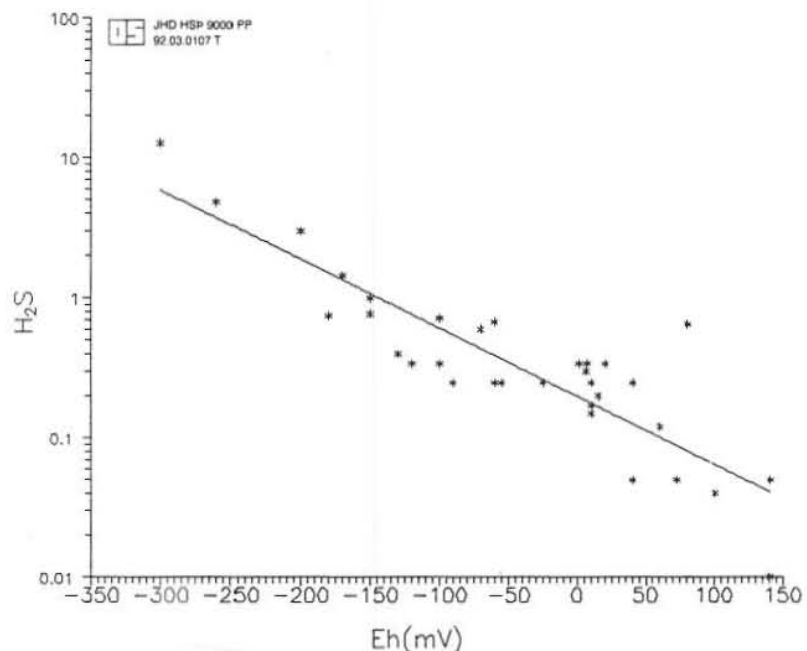
FIGURE 19: Saturation index after heating up to chalcedony geothermometer temperature

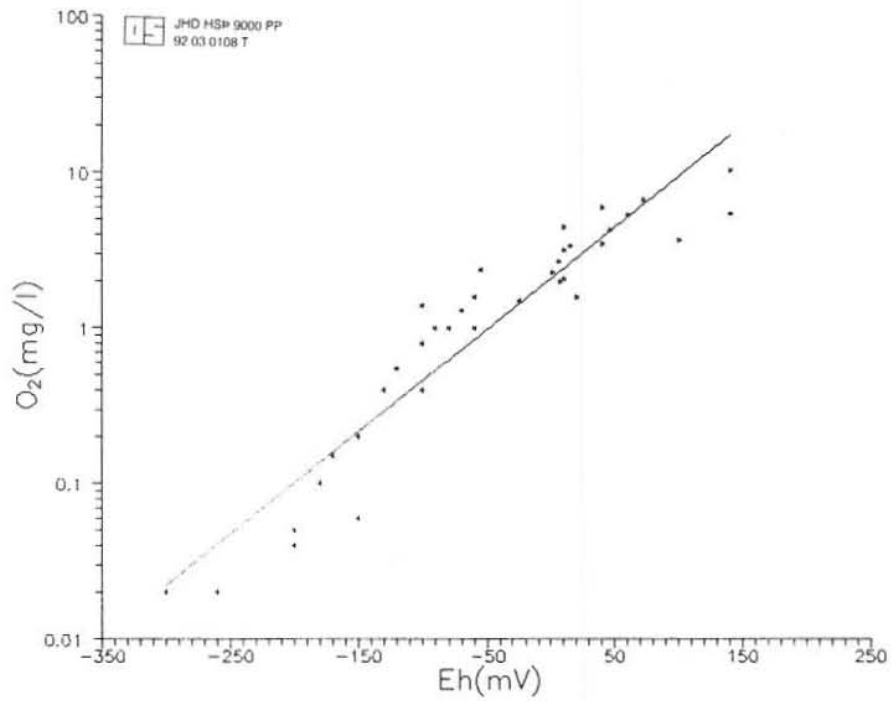
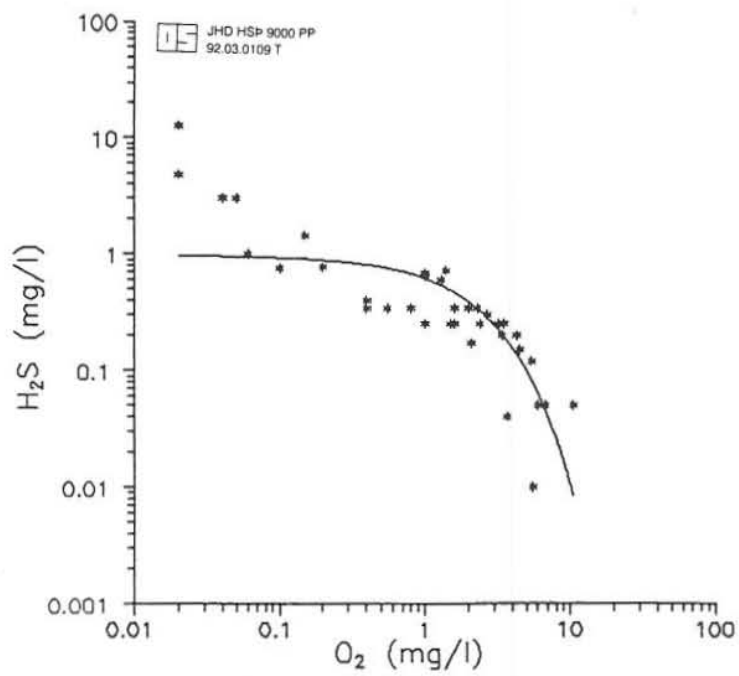
TABLE 7: Quantification of calcite scaling in selected geothermal waters in Serbia

No.	Locality	Q (t/h)	g of $CaCO_3$ /day at T_m	g of $CaCO_3$ /day at $T_{chalcidony}$
1	Vrjci	720	-	-
2	Vrnjci	54	130	292
3	Soko Spa	36	194	260
4	Metkovic	54	194	260
5	Lukovska Spa	72	389	648
6	Bogatic	137	656	902
7	Vranjska Spa	36	280	367

The results of an approximative quantification of calcite scale formation due to heating of spent geothermal waters (during reinjection) are presented in Table 7.

And finally, a short overview on the corrosion potential of selected geothermal waters in Serbia is presented. Data on the chemical composition of the geothermal waters are shown in Table 4. Of 38 water samples, nine have pH below 7, so they have a potential for acid attack (corrosion). The pH of five samples is above 8, so that they have a potential for localized pitting. With one exception the chloride concentration of the geothermal waters is low, does not exceed 150 mg/l. It is known that the threshold of hydrogen sulphide concentration for general corrosion is 0.03 mg/l. The hydrogen sulphide concentration of the selected geothermal waters is in the range of 0.05 to 12.7 mg/l. Lower levels can have a serious effect when oxygen is also present as is the case in geothermal waters in Serbia. The most common carbon dioxide concentration is about 20 mg/l but values as high as 2105 mg/l are observed. Therefore, these geothermal waters are very corrosive due to their carbon dioxide concentration. Furthermore, the pH of geothermal waters with a high carbon dioxide concentration is low (down to 6.29). One of the major species for the estimation of the corrosive properties of geothermal waters is oxygen. In low-temperature geothermal systems, waters usually contain dissolved oxygen in concentrations up to a few mg/l. In the selected geothermal waters in Serbia, the oxygen concentration is from 0.02 up to 10 mg/l. It is known that concentrations up to 0.05 mg/l in hot water cause localized corrosion and pitting. It is obvious that oxygen is present in geothermal waters at concentrations that exceed the desirable value ten to one hundred times and make them extremely corrosive. The hydrogen sulphide concentration as well as the oxygen one are related to the redox potential (Eh). Values of Eh in the selected geothermal waters are in the range from -300 to +140 mV (Figures 20, 21 and 22).

FIGURE 20: Eh versus H_2S concentration

FIGURE 21: *Eh* versus *O*₂ concentrationFIGURE 22: *O*₂ versus *H*₂*S* concentration

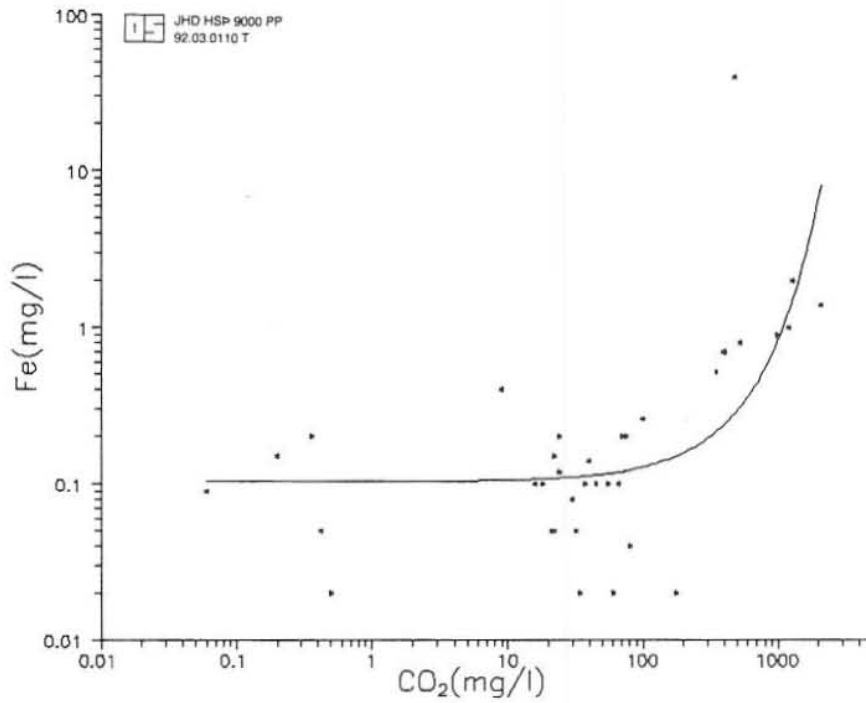


FIGURE 23: *Fe* versus CO_2 concentration

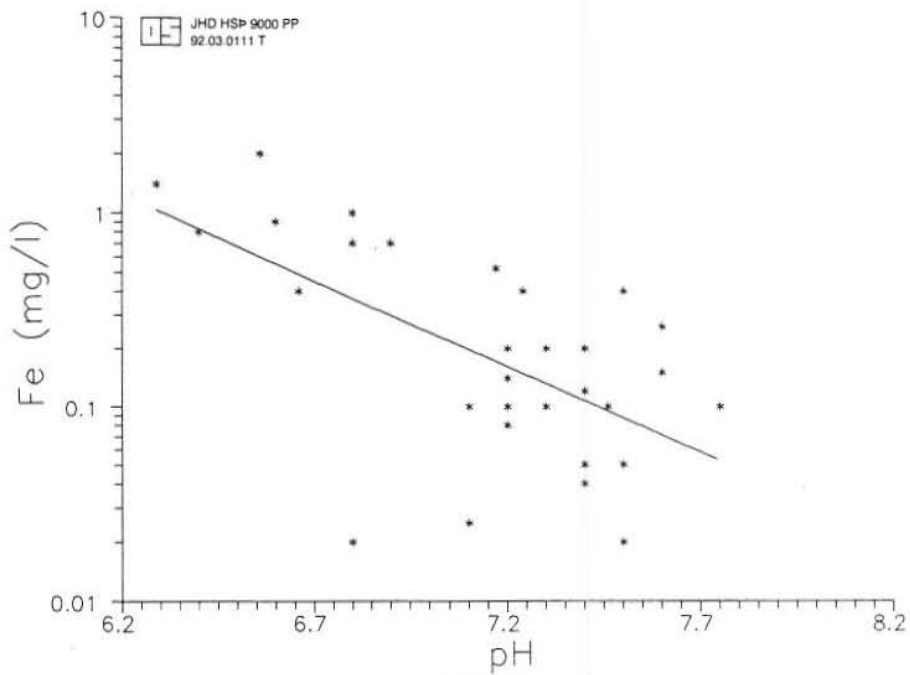


FIGURE 24: *Fe* versus pH

The iron concentration is in the range 0.02 to 2 mg/l and is a function of the carbon dioxide concentration and the pH (Figures 23 and 24). No correlation of iron concentration to those of oxygen and hydrogen sulphide has been found (Figures 25 and 26).

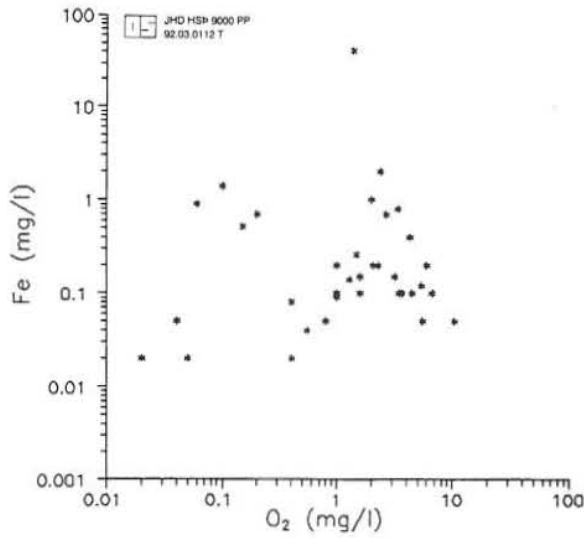


FIGURE 25: *Fe* versus O_2 concentration

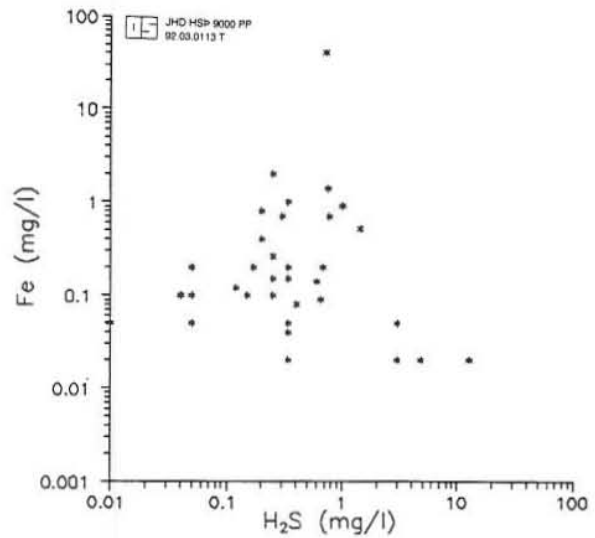


FIGURE 26: *Fe* versus H_2S concentration

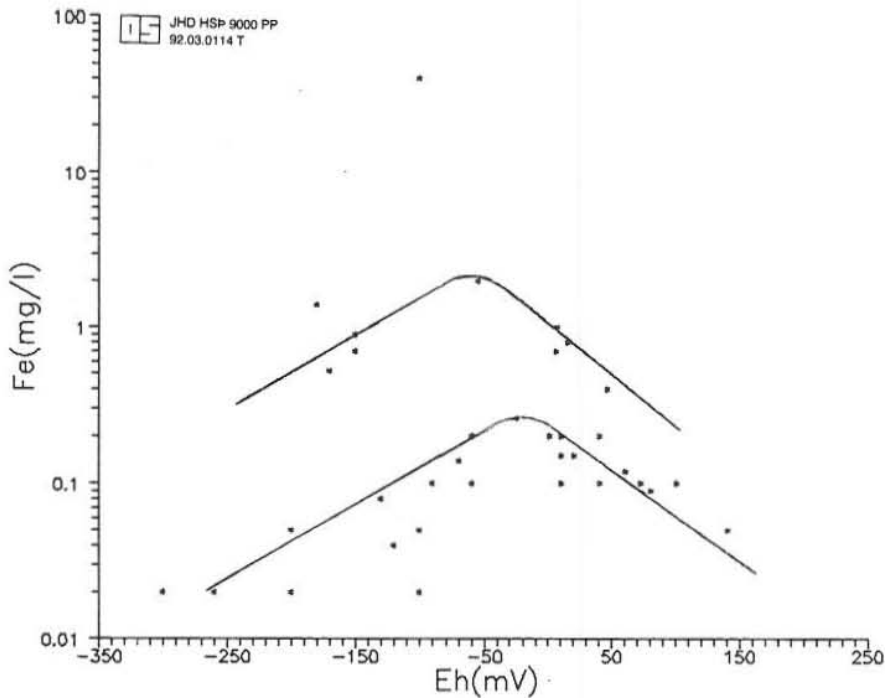


FIGURE 27: *Fe* versus Eh

Figure 27 shows a correlation of iron concentration to redox potential. The upper curve comprises carbon dioxide-rich geothermal waters. Iron concentrations in these waters are high (0.4-2 mg/l). For the other samples the iron concentration ranges from 0.01 to 0.3 mg/l ($Eh = -350 - 0$ mV). Then, by increasing the Eh to +140 mV the iron concentration decreases to 0.05 mg/l. In the first case the iron concentration is controlled by the hydrogen sulphide concentration, while in the second case iron concentration is controlled by the oxygen concentration of the geothermal waters. At high hydrogen sulphide concentrations the corrosion products are mainly iron sulphides but with increasing oxygen concentration iron oxides become the major corrosion products.

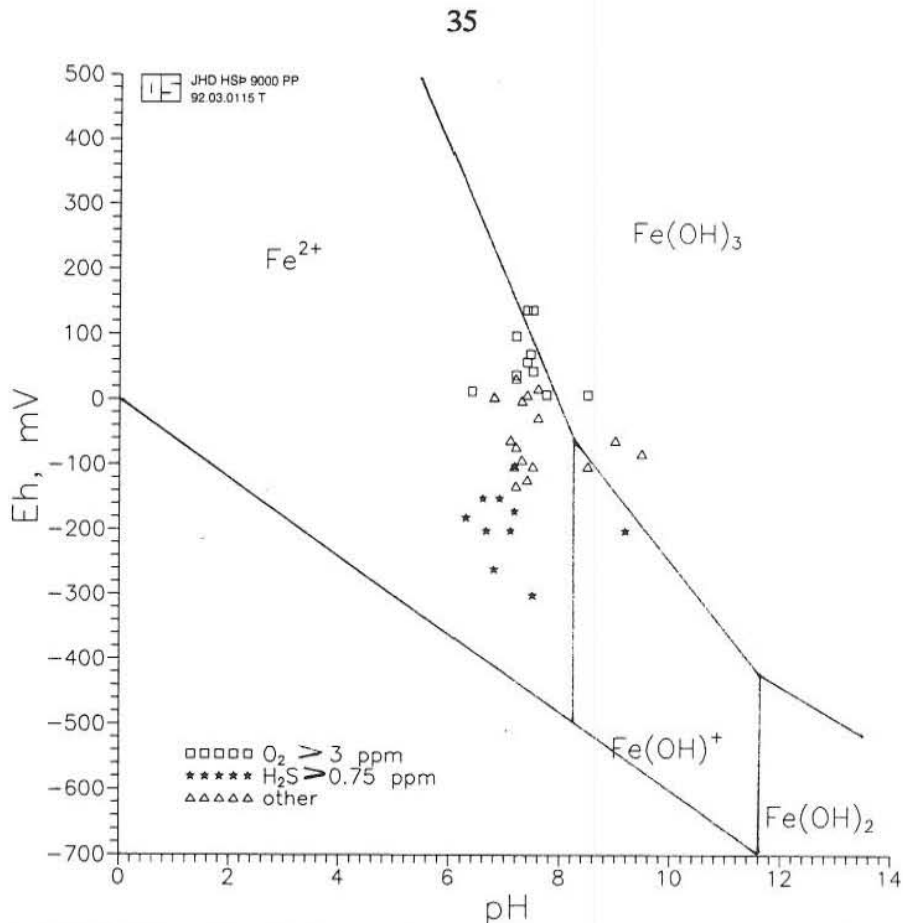


FIGURE 28: *Eh/pH* diagram for selected geothermal waters in Serbia

In Figure 28 a redox potential/*pH* diagram is presented. In this diagram the geothermal waters plot in the stability field of ferrous iron i.e. they can dissolve iron (so they are corrosive). Waters with high hydrogen sulphide concentrations (above 0.75 mg/l) plot at relatively low *Eh* values (down to -300 mV) and the waters of high oxygen concentrations (above 3 mg/l) at relatively high *Eh* values (up to +140 mV). The concentration of iron is usually below 0.1 mg/l and plots very close to the $Fe^{2+}/Fe(OH)_3$ equilibrium line, or in the ferric-hydroxide stability field. These waters only need small changes in *Eh/pH* conditions to move into the ferric-hydroxide stability field (inhibition effect) and scaling may occur.

4.3 Conclusions

From what has been said previously it can be concluded that a knowledge of the chemical composition of geothermal waters is vital for the prediction of the behaviour of materials in a geothermal environment. The general chemical characteristics of geothermal waters in Serbia have been elucidated and from these a prediction of their behaviour in possible exploitation situations has been attempted. The results can be summarized as follows.

Geothermal waters in Serbia are slightly supersaturated with respect to calcite. The saturation index has values up to +0.7. Some of the geothermal waters, mainly those with high carbon dioxide concentrations are undersaturated. Calcite scaling is a potential problem only if a geothermal water boils adiabatically. In the case of conductive cooling this problem is less likely. Adiabatically boiled geothermal waters show supersaturation to a great extent. The saturation

index reaches a value of 1.5. Heating of spent geothermal waters from 25°C up to the measured temperature of the production discharge causes supersaturation with respect to calcite. The saturation index reaches values up to 0.27 and if we want to quantify (approximately) the calcite scale, it turns out to be from 130 to 656 mg $CaCO_3$ /day in the selected wells.

The geothermal waters in Serbia also show a high corrosion potential, which is caused by

- pH values below 7 for 9 samples (total of 38 samples);
- H_2S concentrations in the range of 0.05 to 12.7 mg/l;
- CO_2 concentrations from 20 to 2100 mg/l;
- O_2 concentrations from 0.02 to 10 mg/l;
- iron concentration in geothermal waters that is directly correlated to the pH and the carbon dioxide concentration. The highest iron concentrations are associated with pH below 7 and carbon dioxide concentrations above 300 mg/l. At low Eh values (-300 to -50 mV) the iron concentration is controlled by the hydrogen sulphide concentration, but at higher Eh values (-50 to +140 mV) the iron concentration is controlled by the oxygen concentration.

Generally, the geothermal waters in Serbia are reducing, i.e. in the field of ferrous ion stability, which makes them corrosive. Geothermal waters with oxygen concentrations above 3 mg/l are close to equilibrium with the $Fe(OH)_3$ phase or in the field of ferric hydroxide stability which has an inhibiting effect on corrosion, but promotes scale formation.

Over the last few decades considerable experience has been obtained concerning scaling and corrosion of geothermal waters from various parts of the world. Careful measurements of water quality and systematic analysis of the data allows one to predict potential problems and to plan wells accordingly. For those problems which cannot be anticipated or avoided, there are effective diagnostic tools and corrective measures.

There is still much to learn about the problems in water wells!

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APPENDIX:

Examples of printouts from the WATCH 2 programme; and for
conductive cooling, adiabatic boiling, and heating of spent geothermal water

ORKUSTOFNUN

Lukovska banja

900506011		Lukovska banja,well					
PROGRAM WATCH2.							
WATER SAMPLE (PPM)				STEAM SAMPLE			
PH/DEG.C	6.70/22.0	GAS (VOL.%)		REFERENCE TEMP.	DEGREES C	63.0	
(MEASURED)							
SI02	50.00	CO2		SAMPLING PRESSURE	BARS ABS.		
NA	255.00	H2S		DISCHARGE ENTHALPY	MJOUL/KG		
K	19.00	H2		DISCHARGE	KG/SEC.	20.0	
CA	105.00	O2		MEASURED TEMPERATURE	DEGREES C	63.0	
MG	18.000	CH4		RESISTIVITY/TEMP.	OHMM/DEG.C		
CO2	793.00	N2					
SO4	117.00						
11.0/20.0							
H2S	.01			EH/TEMP.	MV/DEG.C	.000/	
.0							
CL	85.00	LITERS GAS PER KG		MEASURED DOWNHOLE TEMP.	FLUID INFLOW		
F	2.00	CONDENSATE/DEG.C		DEGREES C/METERS	DEPTH		
DISS.SOLIDS	700.00						
AL	.1000						
(METERS)							
B	.3000	CONDENSATE (PPM)		.0	.0	.0	
FE	.5000	PH/DEG.C		.0	.0	.0	
NH3	.1000	CO2		.0	.0	.0	
0		H2S		.0	.0	.0	
0		NA		.0	.0	.0	
0				.0	.0	.0	
				.0	.0	.0	
				.0	.0	.0	
		CONDENSATE WITH NAOH (PPM)		.0	.0	.0	
		CO2		.0	.0	.0	
		H2S		.0	.0	.0	
IONIC STRENGTH =	.02153	IONIC BALANCE :		CATIONS (MOL.EQ.)	.01782728		
				ANIONS (MOL.EQ.)	.01704167		
				DIFFERENCE (%)	4.51		
DEEP WATER (PPM)		DEEP STEAM (PPM)		GAS PRESSURES (BARS)			
ABS.)							
SI02	50.00	CO2	793.00	CO2	.00	CO2	.332E-02
NA	255.00	H2S	.01	H2S	.00	H2S	.340E-07
K	19.00	H2	.00	H2	.00	H2	.000E+00
CA	105.00	O2	.00	O2	.00	O2	.000E+00
MG	17.999	CH4	.00	CH4	.00	CH4	.000E+00
SO4	117.00	N2	.00	N2	.00	N2	.000E+00
CL	84.99	NH3	.10	NH3	.00	NH3	.121E-09
F	2.00					H2O	.228E+00
DISS.S.	700.00					TOTAL	.232E+00
AL	.1000						
B	.3000			H2O (%)	.00		
FE	.5000			BOILING PORTION	.00		

ACTIVITY COEFFICIENTS IN DEEP WATER

H+	.880	KSO4-	.865	FE++	.571	FECL+	.858
OH-	.856	F-	.856	FE+++	.323	AL+++	.323
H3SIO4-	.858	CL-	.853	FEOH+	.863	ALOH++	.564
H2SIO4--	.564	NA+	.858	FE(OH)3-	.863	AL(OH)2+	.865
H2BO3-	.850	K+	.853	FE(OH)4--	.559	AL(OH)4-	.861
HCO3-	.858	CA++	.571	FEOH++	.559	ALSO4+	.861
CO3--	.553	MG++	.594	FE(OH)2+	.865	AL(SO4)2-	.861
HS-	.856	CAHCO3+	.868	FE(OH)4-	.865	ALF++	.564
S--	.559	MGHCO3+	.858	FESO4+	.863	ALF2+	.865
HSO4-	.861	CAOH+	.868	FECL++	.559	ALF4-	.861
SO4--	.546	MGOH+	.870	FECL2+	.863	ALF5--	.553
NASO4-	.865	NH4+	.850	FECL4-	.858	ALF6---	.264

CHEMICAL COMPONENTS IN DEEP WATER (PPM AND LOG MOLE)

H+ (ACT.)	.00	-6.599	MG++	14.11	-3.236	FE(OH)3	.00	-11.735
OH-	.01	-6.289	NACL	.09	-5.794	FE(OH)4-	.00	-12.672
H4SIO4	79.79	-3.081	KCL	.00	-7.373	FECL+	.00	-7.715
H3SIO4-	.18	-5.734	NASO4-	1.93	-4.790	FECL2	.00	-24.026
H2SIO4--	.00	-10.183	KSO4-	.42	-5.510	FECL++	.00	-21.163
NAH3SIO4	.02	-6.713	CASO4	15.23	-3.951	FECL2+	.00	-23.378
H3BO3	1.71	-4.559	MGSO4	11.25	-4.029	FECL3	.00	-26.931
H2BO3-	.01	-6.934	CACO3	1.22	-4.913	FECL4-	.00	-31.170
H2CO3	336.59	-2.265	MGCO3	.14	-5.792	FESO4	.07	-6.310
HCO3-	736.52	-1.918	CAHCO3+	44.33	-3.358	FESO4+	.00	-19.383
CO3--	.32	-5.271	MGHCO3+	5.52	-4.189	AL+++	.00	-12.232
H2S	.01	-6.809	CAOH+	.00	-7.833	ALOH++	.00	-9.374
HS-	.00	-6.859	MGOH+	.00	-7.352	AL(OH)2+	.01	-6.983
S--	.00	-16.589	NH4OH	.00	-6.903	AL(OH)3	.18	-5.628
H2SO4	.00	-16.364	NH4+	.10	-5.241	AL(OH)4-	.12	-5.915
HSO4-	.00	-7.319	FE++	.46	-5.080	ALSO4+	.00	-12.668
SO4--	95.37	-3.003	FE+++	.00	-20.445	AL(SO4)2-	.00	-13.953
HF	.00	-7.148	FEOH+	.01	-6.910	ALF++	.00	-9.375
F-	2.00	-3.978	FE(OH)2	.00	-10.376	ALF2+	.00	-7.847
CL-	84.93	-2.621	FE(OH)3-	.00	-15.352	ALF3	.00	-7.841
NA+	254.59	-1.956	FE(OH)4--	.00	-22.033	ALF4-	.00	-9.412
K+	18.88	-3.316	FE(OH)++	.00	-15.634	ALF5--	.00	-11.932
CA++	82.45	-2.687	FE(OH)2+	.00	-12.788	ALF6---	.00	-15.289

IONIC STRENGTH = .02061 IONIC BALANCE : CATIONS (MOL.EQ.) .01735803
 ANIONS (MOL.EQ.) .01657125
 DIFFERENCE (%) 4.64

CHEMICAL GEOTHERMOMETERS DEGREES C

1000/T DEGREES KELVIN = 2.97

QUARTZ 97.0
 CHALCEDONY 71.9
 NAK 171.0

OXIDATION POTENTIAL (VOLTS) : EH H2S= -.225 EH CH4= 99.999 EH H2= 99.999 EH NH3= 99.999

LOG SOLUBILITY PRODUCTS OF MINERALS IN DEEP WATER

	TEOR.	CALC.		TEOR.	CALC.		TEOR.	CALC.
ADULARIA	-18.929	-18.124	ALBITE LOW	-18.044	-16.761	ANALCIME	-14.373	-13.680
ANHYDRITE	-5.118	-6.195	CALCITE	-8.877	-8.458	CHALCEDONY	-3.165	-3.081
MG-CHLORITE	-81.960	-88.400	FLUORITE	-10.656	-11.021	GOETHITE	-5.988	-6.379
LAUMONTITE	-29.287	-26.245	MICROCLINE	-20.596	-18.124	MAGNETITE	-32.529	-30.793
CA-MONTMOR.	-96.576	-71.373	K-MONTMOR.	-47.597	-37.607	MG-MONTMOR.	-97.516	-71.906
NA-MONTMOR.	-47.464	-36.244	MUSCOVITE	-23.832	-16.403	PREHNITE	-38.454	-38.808
PYRRHOTITE	-118.384	-121.758	PYRITE	-175.068	-143.717	QUARTZ	-3.484	-3.081
WAIKAKITE	-25.950	-26.245	WOLLASTONITE	12.089	7.187	ZOISITE	-37.233	-37.947
EPIDOTE	-46.627	-45.186	MARCASITE	-149.083	-143.717			

ORKUSTOFNUN
SAMPLE = 900506011

DEEP WATER COOLED TO 25.0 DEGREES C.

ACTIVITY COEFFICIENTS IN DEEP WATER

H+	.887	KSO4-	.873	FE++	.590	FECL+	.866
OH-	.864	F-	.864	FE+++	.344	AL+++	.344
H3SiO4-	.866	CL-	.861	FEOH+	.871	ALOH++	.583
H2SiO4--	.583	NA+	.866	FE(OH)3-	.871	AL(OH)2+	.873
H2BO3-	.858	K+	.861	FE(OH)4--	.578	AL(OH)4-	.869
HCO3-	.866	CA++	.590	FEOH++	.578	ALSO4+	.869
CO3--	.572	MG++	.612	FE(OH)2+	.873	AL(SO4)2-	.869
HS-	.864	CAHCO3+	.875	FE(OH)4-	.873	ALF++	.583
S--	.578	MGHCO3+	.866	FESO4+	.871	ALF2+	.873
HSO4-	.869	CAOH+	.875	FECL++	.578	ALF4-	.869
SO4--	.566	MGOH+	.877	FECL2+	.871	ALF5--	.572
NASO4-	.873	NH4+	.858	FECL4-	.866	ALF6---	.286

CHEMICAL COMPONENTS IN DEEP WATER (PPM AND LOG MOLE)

H+ (ACT.)	.00	-6.686	MG++	15.53	-3.195	FE(OH)3	.00	-14.616
OH-	.00	-7.240	NACL	.03	-6.263	FE(OH)4-	.00	-16.170
H4SiO4	79.93	-3.080	KCL	.00	-7.600	FECL+	.00	-8.321
H3SiO4-	.05	-6.246	NASO4-	1.35	-4.947	FECL2	.00	-28.721
H2SiO4--	.00	-11.117	KSO4-	.27	-5.699	FECL++	.00	-22.102
NAH3SiO4	.01	-7.181	CASO4	12.25	-4.046	FECL2+	.00	-24.315
H3BO3	1.71	-4.558	MGSO4	5.31	-4.355	FECL3	.00	-28.060
H2BO3-	.01	-7.076	CACO3	.44	-5.353	FECL4-	.00	-32.603
H2CO3	335.84	-2.266	MGCO3	.07	-6.062	FESO4	.07	-6.319
HCO3-	754.27	-1.908	CAHCO3+	17.93	-3.751	FESO4+	.00	-20.142
CO3--	.24	-5.392	MGHCO3+	4.84	-4.246	AL+++	.00	-9.943
H2S	.01	-6.709	CAOH+	.00	-8.885	ALOH++	.00	-8.216
HS-	.00	-7.010	MGOH+	.00	-8.455	AL(OH)2+	.01	-6.895
S--	.00	-17.220	NH4OH	.00	-7.853	AL(OH)3	.06	-6.128
H2SO4	.00	-17.557	NH4+	.11	-5.232	AL(OH)4-	.02	-6.621
HSO4-	.00	-7.843	FE++	.47	-5.073	ALSO4+	.00	-10.553
SO4--	102.79	-2.971	FE+++	.00	-20.661	AL(SO4)2-	.00	-11.881
HF	.00	-7.559	FEOH+	.00	-7.886	ALF++	.00	-7.255
F-	1.95	-3.989	FE(OH)2	.00	-12.510	ALF2+	.09	-5.873
CL-	84.97	-2.620	FE(OH)3-	.00	-18.914	ALF3	.10	-5.934
NA+	254.73	-1.955	FE(OH)4--	.00	-26.439	ALF4-	.00	-7.545
K+	18.92	-3.315	FE(OH)++	.00	-16.650	ALF5--	.00	-10.066
CA++	94.11	-2.629	FE(OH)2+	.00	-14.843	ALF6---	.00	-13.316

IONIC STRENGTH = .02147 IONIC BALANCE : CATIONS (MOL.EQ.) .01779549
 ANIONS (MOL.EQ.) .01700993
 DIFFERENCE (%) 4.51

OXIDATION POTENTIAL (VOLTS) : EH H2S= -.167 EH CH4= 99.999 EH H2= 99.999 EH NH3= 99.999

LOG SOLUBILITY PRODUCTS OF MINERALS IN DEEP WATER

	TEOR.	CALC.		TEOR.	CALC.		TEOR.	CALC.
ADULARIA	-21.303	-18.113	ALBITE LOW	-20.211	-16.751	ANALCIME	-16.023	-13.670
ANHYDRITE	-4.709	-6.076	CALCITE	-8.490	-8.493	CHALCEDONY	-3.583	-3.080
MG-CHLORITE	-85.227	-95.697	FLUORITE	-10.966	-10.963	GOETHITE	-7.286	-8.926
LAUMONTITE	-32.295	-26.163	MICROCLINE	-23.329	-18.113	MAGNETITE	-35.665	-37.761
CA-MONTMOR.	-111.461	-59.867	K-MONTMOR.	-55.613	-31.884	MG-MONTMOR.	-112.104	-60.417
NA-MONTMOR.	-55.264	-30.522	MUSCOVITE	-27.505	-14.490	PREHNITE	-41.206	-40.549
PYRRHOTITE	-138.252	-143.173	PYRITE	-207.357	-160.644	QUARTZ	-3.980	-3.080
WAIKAKITE	-27.894	-26.163	WOLLASTONITE	13.720	7.433	ZOISITE	-39.612	-38.738
EPIDOTE	-50.254	-49.475	MARCASITE	-178.077	-160.644			

ORKUSTOFNUN
SAMPLE = 900506011

DEEP WATER BOILED AT 25.0 DEGREES C.

LOG DISTRIBUTION COEFFICIENTS		CO2 = -2.67	H2S = -2.25	GAS SOLUBILITY MULTIPLYING FACTOR			
.01							
DEEP WATER (PPM)		DEEP STEAM (PPM)		GAS PRESSURES (BARS)			
ABS.)							
SIO2	53.49	CO2	588.21	CO2	3730.53	CO2	.482E-04
NA	272.78	H2S	.01	H2S	.07	H2S	.111E-08
K	20.32	H2	.00	H2	.00	H2	.000E+00
CA	112.32	O2	.00	O2	.00	O2	.000E+00
MG	19.253	CH4	.00	CH4	.00	CH4	.000E+00
SO4	125.15	N2	.00	N2	.00	N2	.000E+00
CL	90.92	NH3	.11	NH3	.00	NH3	.919E-10
F	2.14					H2O	.316E-01
DISS.S.	748.80					TOTAL	.316E-01
AL	.1070						
B	.3209			H2O (%)	6.52		
FE	.5349			BOILING PORTION	.07		

ACTIVITY COEFFICIENTS IN DEEP WATER

H+	.884	KSO4-	.869	FE++	.582	FECL+	.863
OH-	.860	F-	.860	FE+++	.335	AL+++	.335
H3SIO4-	.863	CL-	.857	FEOH+	.867	ALOH++	.575
H2SIO4--	.575	NA+	.863	FE(OH)3-	.867	AL(OH)2+	.869
H2BO3-	.854	K+	.857	FE(OH)4--	.570	AL(OH)4-	.865
HCO3-	.863	CA++	.582	FEOH++	.570	ALSO4+	.865
CO3--	.563	MG++	.604	FE(OH)2+	.869	AL(SO4)2-	.865
HS-	.860	CAHCO3+	.872	FE(OH)4-	.869	ALF++	.575
S--	.570	MGHCO3+	.863	FESO4+	.867	ALF2+	.869
HSO4-	.865	CAOH+	.872	FECL++	.570	ALF4-	.865
SO4--	.557	MGOH+	.874	FECL2+	.867	ALF5--	.563
NASO4-	.869	NH4+	.854	FECL4-	.863	ALF6---	.276

CHEMICAL COMPONENTS IN DEEP WATER (PPM AND LOG MOLE)

H+ (ACT.)	.00	-8.165	MG++	16.01	-3.182	FE(OH)3	.00	-11.865
OH-	.03	-5.760	NACL	.04	-6.209	FE(OH)4-	.00	-11.939
H4SIO4	83.62	-3.060	KCL	.00	-7.546	FECL+	.00	-8.288
H3SIO4-	1.71	-4.746	NASO4-	1.52	-4.895	FECL2	.00	-28.662
H2SIO4--	.00	-8.134	KSO4-	.30	-5.647	FECL++	.00	-23.753
NAH3SIO4	.26	-5.655	CASO4	12.93	-4.022	FECL2+	.00	-25.944
H3BO3	1.68	-4.566	MGSO4	5.69	-4.325	FECL3	.00	-29.663
H2BO3-	.15	-5.603	CACO3	13.68	-3.864	FECL4-	.00	-34.177
H2CO3	11.37	-3.737	MGCO3	2.28	-4.568	FESO4	.08	-6.293
HCO3-	771.96	-1.898	CAHCO3+	18.40	-3.740	FESO4+	.00	-21.803
CO3--	7.58	-3.899	MGHCO3+	5.05	-4.228	AL+++	.00	-14.672
H2S	.00	-7.956	CAOH+	.00	-7.403	ALOH++	.00	-11.471
HS-	.01	-6.777	MGOH+	.00	-6.967	AL(OH)2+	.00	-8.676
S--	.00	-15.504	NH4OH	.01	-6.377	AL(OH)3	.03	-6.432
H2SO4	.00	-20.492	NH4+	.11	-5.233	AL(OH)4-	.34	-5.445
HSO4-	.00	-9.297	FE++	.48	-5.062	ALSO4+	.00	-15.269
SO4--	110.00	-2.941	FE+++	.00	-22.335	AL(SO4)2-	.00	-16.574
HF	.00	-8.999	FEOH+	.03	-6.401	ALF++	.00	-11.950
F-	2.14	-3.948	FE(OH)2	.00	-9.549	ALF2+	.00	-10.534
CL-	90.89	-2.591	FE(OH)3-	.00	-14.472	ALF3	.00	-10.559
NA+	272.42	-1.926	FE(OH)4--	.00	-20.514	ALF4-	.00	-12.130
K+	20.23	-3.286	FE(OH)++	.00	-16.850	ALF5--	.00	-14.607
CA++	95.74	-2.622	FE(OH)2+	.00	-13.569	ALF6---	.00	-17.811

IONIC STRENGTH = .02264 IONIC BALANCE : CATIONS (MOL.EQ.) .01872607
ANIONS (MOL.EQ.) .01789627
DIFFERENCE (%) 4.53

OXIDATION POTENTIAL (VOLTS) : EH H2S= -.267 EH CH4= 99.999 EH H2= 99.999 EH NH3= 99.999

LOG SOLUBILITY PRODUCTS OF MINERALS IN DEEP WATER

	TEOR.	CALC.		TEOR.	CALC.		TEOR.	CALC.
ADULARIA	-21.303	-17.999	ALBITE LOW	-20.211	-16.637	ANALCIME	-16.023	-13.576
ANHYDRITE	-4.709	-6.052	CALCITE	-8.490	-7.005	CHALCEDONY	-3.583	-3.060
MG-CHLORITE	-85.227	-83.714	FLUORITE	-10.966	-10.885	GOETHITE	-7.286	-6.175
LAUMONTITE	-32.295	-26.028	MICROCLINE	-23.329	-17.999	MAGNETITE	-35.665	-29.298
CA-MONTMOR.	-111.461	-76.791	K-MONTMOR.	-55.613	-40.320	MG-MONTMOR.	-112.104	-77.335
NA-MONTMOR.	-55.264	-38.958	MUSCOVITE	-27.505	-17.278	PREHNITE	-41.206	-37.476
PYRRHOTITE	-138.252	-129.462	PYRITE	-207.357	-160.290	QUARTZ	-3.980	-3.060
WAIKAKITE	-27.894	-26.028	WOLLASTONITE	13.720	10.412	ZOISITE	-39.612	-37.115
EPIDOTE	-50.254	-43.651	MARCASITE	-178.077	-160.290			

ORKUSTOFNUN

lukovska banja

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900506011          Lukovska banja,well

PROGRAM WATCH2.

WATER SAMPLE (PPM)          STEAM SAMPLE

PH/DEG.C          9.53/25.0  GAS (VOL.%)          REFERENCE TEMP.          DEGREES C          100.0
(ARBITRARY)
SI02              53.50      CO2
NA                272.80     H2S
K                 20.30      H2
CA                .53       O2
MG                19.250     CH4
CO2               343.50     N2
SO4               125.00
11.0/20.0
H2S              .01
.0
CL                90.00
F                  2.00      LITERS GAS PER KG
DISS.SOLIDS      700.00     CONDENSATE/DEG.C          MEASURED DOWNHOLE TEMP.  FLUID INFLOW
AL                .1000     DEGREES C/METERS          DEPTH
(METERS)
B                 .3000
FE                .5000     CONDENSATE (PPM)          .0          .0          .0
NH3              .1000     PH/DEG.C                  .0          .0          .0
O                 0          CO2                        .0          .0          .0
O                 0          H2S                        .0          .0          .0
O                 0          NA                          .0          .0          .0
.0          .0          .0          .0          .0
.0          .0          .0          .0          .0
.0          .0          .0          .0          .0
.0          .0          .0          .0          .0
CONDENSATE WITH NAOH (PPM)  .0          .0          .0
CO2               .0          .0          .0
H2S               .0          .0          .0

IONIC STRENGTH = .01697      IONIC BALANCE :  CATIONS (MOL.EQ.) .01335748
ANIONS (MOL.EQ.) .01436612
DIFFERENCE (%)    -7.28

DEEP WATER (PPM)          DEEP STEAM (PPM)          GAS PRESSURES (BARS
ABS.)
SI02              53.50      CO2              343.50     CO2              .00          CO2              .180E-02
NA                272.80     H2S              .01          H2S              .00          H2S              .399E-07
K                 20.30      H2               .00          H2               .00          H2               .000E+00
CA                .53       O2               .00          O2               .00          O2               .000E+00
MG                19.248     CH4              .00          CH4              .00          CH4              .000E+00
SO4               125.00     N2               .00          N2               .00          N2               .000E+00
CL                89.99     NH3              .10          NH3              .00          NH3              .184E-05
F                  2.00
DISS.S.           700.00
AL                .1000
B                 .3000
FE                .5000
H2O (%)          .00
BOILING PORTION  .00

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ACTIVITY COEFFICIENTS IN DEEP WATER

H+	.881	KSO4-	.868	FE++	.576	FECL+	.862
OH-	.859	F-	.859	FE+++	.325	AL+++	.325
H3SiO4-	.862	CL-	.857	FEOH+	.866	ALOH++	.570
H2SiO4--	.570	NA+	.862	FE(OH)3-	.866	AL(OH)2+	.868
H2BO3-	.854	K+	.857	FE(OH)4--	.565	AL(OH)4-	.864
HCO3-	.862	CA++	.576	FEOH++	.565	ALSO4+	.864
CO3--	.559	MG++	.597	FE(OH)2+	.868	AL(SO4)2-	.864
HS-	.859	CAHCO3+	.870	FE(OH)4-	.868	ALF++	.570
S--	.565	MGHCO3+	.862	FESO4+	.866	ALF2+	.868
HSO4-	.864	CAOH+	.870	FECL++	.565	ALF4-	.864
SO4--	.554	MGOH+	.872	FECL2+	.866	ALF5--	.559
NASO4-	.868	NH4+	.854	FECL4-	.862	ALF6---	.271

CHEMICAL COMPONENTS IN DEEP WATER (PPM AND LOG MOLE)

H+ (ACT.)	.00	-8.942	MG++	8.36	-3.463	FE(OH)3	.01	-7.035
OH-	9.54	-3.251	NACL	.28	-5.315	FE(OH)4-	.90	-5.140
H4SiO4	38.48	-3.398	KCL	.01	-7.083	FECL+	.00	-9.484
H3SiO4-	41.48	-3.360	NASO4-	3.71	-4.506	FECL2	.00	-22.545
H2SiO4--	.55	-5.230	KSO4-	.85	-5.202	FECL++	.00	-25.238
NAH3SiO4	5.67	-4.318	CASO4	.06	-6.378	FECL2+	.00	-27.398
H3BO3	.79	-4.894	MGSO4	17.66	-3.834	FECL3	.00	-30.753
H2BO3-	.91	-4.824	CACO3	.79	-5.103	FECL4-	.00	-34.716
H2CO3	1.06	-4.767	MGCO3	19.15	-3.644	FESO4	.00	-8.429
HCO3-	417.50	-2.165	CAHCO3+	.12	-5.930	FESO4+	.00	-23.491
CO3--	40.80	-3.168	MGHCO3+	2.55	-4.525	AL+++	.00	-23.643
H2S	.00	-8.953	CAOH+	.00	-7.350	ALOH++	.00	-17.381
HS-	.01	-6.534	MGOH+	1.82	-4.355	AL(OH)2+	.00	-11.649
S--	.00	-13.490	NH4OH	.20	-5.245	AL(OH)3	.00	-7.434
H2SO4	.00	-20.026	NH4+	.00	-6.724	AL(OH)4-	.35	-5.435
HSO4-	.00	-9.099	FE++	.00	-7.376	ALSO4+	.00	-23.731
SO4--	107.27	-2.952	FE+++	.00	-25.276	AL(SO4)2-	.00	-24.836
HF	.00	-9.148	FEOH+	.07	-6.037	ALF++	.00	-20.484
F-	2.00	-3.978	FE(OH)2	.06	-6.204	ALF2+	.00	-18.701
CL-	89.82	-2.596	FE(OH)3-	.00	-7.673	ALF3	.00	-18.551
NA+	270.87	-1.929	FE(OH)4--	.00	-11.432	ALF4-	.00	-20.046
K+	20.05	-3.290	FE(OH)++	.00	-17.331	ALF5--	.00	-22.558
CA++	.15	-5.433	FE(OH)2+	.00	-11.163	ALF6---	.00	-26.036

IONIC STRENGTH = .01574

IONIC BALANCE :

CATIONS (MOL.EQ.) .01306656

ANIONS (MOL.EQ.) .01410878

DIFFERENCE (%) -7.67

CHEMICAL GEOTHERMOMETERS DEGREES C

1000/T DEGREES KELVIN = 2.68

QUARTZ	66.8
CHALCEDONY	40.7
NAK	170.9

OXIDATION POTENTIAL (VOLTS) : EH H2S= -.482 EH CH4= 99.999 EH H2= 99.999 EH NH3= 99.999

LOG SOLUBILITY PRODUCTS OF MINERALS IN DEEP WATER

	TEOR.	CALC.		TEOR.	CALC.		TEOR.	CALC.
ADULARIA	-17.222	-19.044	ALBITE LOW	-16.485	-17.681	ANALCIME	-13.199	-14.283
ANHYDRITE	-5.607	-8.881	CALCITE	-9.438	-9.092	CHALCEDONY	-2.841	-3.398
MG-CHLORITE	-80.302	-66.158	FLUORITE	-10.538	-13.759	GOETHITE	-4.674	-1.884
LAUMONTITE	-27.182	-30.252	MICROCLINE	-18.598	-19.044	MAGNETITE	-29.703	-18.018
CA-MONTMOR.	-85.561	-117.536	K-MONTMOR.	-41.649	-59.289	MG-MONTMOR.	-86.709	-115.551
NA-MONTMOR.	-41.659	-57.925	MUSCOVITE	-21.151	-23.399	PREHNITE	-36.778	-39.161
PYRRHOTITE	-99.806	-99.079	PYRITE	-147.012	-145.948	QUARTZ	-3.098	-3.398
WAIRAKITE	-24.710	-30.252	WOLLASTONITE	10.824	8.814	ZOISITE	-35.893	-41.338
EPIDOTE	-43.602	-41.045	MARCASITE	-123.575	-145.948			