

CHEMICAL INTERPRETATION AND SCALING POTENTIAL IN ORADEA GEOTHERMAL AREA, ROMANIA

Oana Stănășel*, Hrefna Kristmannsdottir**, Ludovic Gilău*

*University of Oradea
5 Armatei Romane
3700 Oradea, Romania

**Orkustofnun
Grensasvegur 9
108 Reykjavik, Iceland

ABSTRACT

Felix geothermal resort located at about 6 km to Oradea is the most useful place for balneological treatment in Romania. Geothermal water from Felix was sampled and analysed in the chemical laboratory from Orkustofnun, Iceland. A geothermal well used for district heating in Oradea was also chosen for study. Water was sampled and analysed in Orkustofnun as well.

The $\text{Cl-SO}_4\text{-HCO}_3$ triangular diagram (by Gigenbach and Arnorsson) classified these geothermal waters. Geothermometry was used for the determination of subsurface or reservoir temperature by assuming equilibrium between specific minerals and the geothermal fluids at depth. The silica-enthalpy mixing model was applied.

Calculations were performed using an aqueous speciation program of Bjarnason to construct the mineral equilibrium diagram showing the saturation index from the measured temperature to 30-40°C for samples in Oradea geothermal field. Solid depositions formed during utilization were analysed by XRD analysis.

INTRODUCTION

Considering the outstanding special therapeutic properties of the geothermal water from Felix Spa this thermomineral water was taken for analysis. Due to scaling problems recorded there were made depositions analysis and it was predicted the potential scale under the conditions of utilisation.

The geothermal energy from Nufăr provides heating for more than 2000 flats and some administrative buildings. Based on good analytical results, thermodynamic data on different minerals which could start to precipitate could be obtained.

BRIEF DESCRIPTION OF THE STUDIED AREA

The resort of Felix lies at an altitude of 140 m in the north-western part of the country, near the frontier

with Hungary. It is characterized by a continental temperate climate. The waters, which spring up at Felix, come from the lower cretaceous system. In a zone of the thermal lake grows a plant belonging to the lotus family, a variety unique in Europe and at the same time a relic of the flora of the tertiary era.

The objects found in the resort on the occasion of various diggings attests the fact that Romans knew the thermal mineral waters at Felix. The waters were awarded the gold medal at the 1896 exhibition. After the second world war, the resort had a rapid development. The rhythm of modernization of the hotels and treatment base in the last years is one of the most impetuous, the resort having completely changed its appearance.

Felix Spa has a large experience in treating degenerative and inflammatory rheumatism – an experience based on a cure methodology specific to this resort. As a result of the medical research and experiments the following diseases are treated at Felix: chronic inflammatory rheumatism, rheumatismal degenerative diseases, post-traumatic diseases, troubles of the nervous system, associated diseases of the main profiles mentioned above. A modern polyclinic with balneological treatment including baths with thermal water has been functioned at Felix for about ten years. Geothermal water used in this polyclinic was taken for study.

The Oradea aquifer is located in Triassic limestone and dolomites and it is exploited by 12 wells with a total artesian flow rate of 140 l/s geothermal water with wellhead temperatures of 70-105°C. Well 4797 from Nufăr is a production well with a total discharge of 32 l/s. This well supplies the space heating of more than 2000 flats from Oradea. The whole amount of waste geothermal water at a return temperature of 30°C is reinjected in well 4081 to keep the pressure in the reservoir. This dublet has been using for about 15 years. Geothermal water from the production well was sampled and analysed.

CLASSIFICATION OF THE GEOTHERMAL WATERS

Water samples were collected from Felix and Nufăr in July 2001. They were analysed in Orkustofnun laboratory from Iceland. All the methods used are listed in Table 1.

Table 1. Orkustofnun geochemical laboratory from Iceland; methods of chemical analysis

Constituent	Methodology
pH	Glass electrode pH meter
SiO ₂	UV/VIS silico-molybdate complex
B	Spectrophotometry at 420 nm; azomethine H/ ascorbic acid reagent added
Na	Atomic absorption spectrometry with cesium as inhibitor
K	Atomic absorption spectrometry with cesium as inhibitor
Ca	Atomic absorption spectrometry with La as inhibitor
Mg	Atomic absorption spectrometry with La as inhibitor
Al	Atomic absorption spectrometry with graphite furnace
Fe	Atomic absorption spectrometry with graphite furnace
F	pH milivoltmeter and selective electrode ORION Model 96-09
Cl	Ion chromatography; borax eluent
SO ₄	Ion chromatography; using a mixture of Na ₂ CO ₃ and NaHCO ₃ as eluent
CO ₂	Electrometric titration
TDS	Gravimetric

The results of the laboratory analysis are summarized in Table 2. The wellhead temperatures measured during sampling were: 42°C at Felix and 71°C at Nufăr. The ionic balances for the samples calculated by the Watch program gave values acceptable for equilibrium calculations: -2.02 at Felix and -0.01 at Nufăr; the data could be used for interpretation.

As seen from the Table 2 the geothermal waters from Felix are slightly basic. The sulphate concentration is very high in Nufăr. The mineralisation of water from Felix is very low. The chloride content is low in both of the wells.

Table 2. Chemical composition of geothermal waters, in mg/l.

Component	Well Felix	Well Nufăr
pH	8	7.2
CO ₂	280.55	179.44
B	0.18	0.05
SiO ₂	21.6	41.3
Na	15.44	177.26
K	4.45	13.17
Mg	19.53	63.34
Ca	120.4	274.6
F	0.465	1.182
Cl	9.8	7.47
SO ₄	92	1107.6
Al	0.001	0.005
Fe	0.013	0.061
TDS	452	1508

For an initial classification, in terms of the major anions Cl, SO₄ and bicarbonate, a triangular diagram (Giggenbach, 1991) was used. The position of a data point in this diagram is simply obtained by first finding the sum of the concentrations (in mg/l) of all three constituents involved. The next step consists of the evaluation of %Cl, %SO₄ and %HCO₃. The triangular diagram Cl-SO₄-HCO₃ (Figure 1) for romanian geothermal waters indicate that the bicarbonate content of waters from Felix is high. The geothermal water from Nufăr seems to be a steam heated water, that means that we might expect some boiling in the reservoir, so the hydrogen sulphide will transform into sulphate. From Table 2 they can notice the high sulphate concentration in geothermal water from Nufăr.

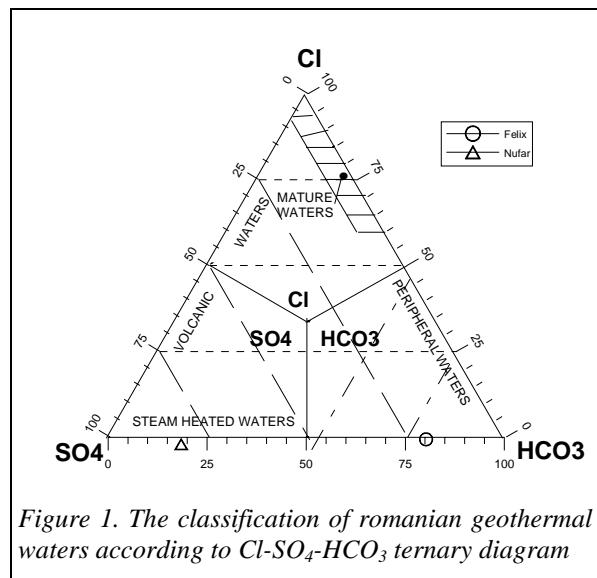


Figure 1. The classification of romanian geothermal waters according to Cl-SO₄-HCO₃ ternary diagram

The Na-K-Mg triangular diagram is also obtained in analogous manner with the Cl-SO₄-HCO₃ diagram and the position of a data point on the diagram is calculated similarly (Figure 2). Waters from Felix and Nufăr seems to have a high percent of Mg content, but it would be inaccurate to use waters plotting in the

immature region, implying that these waters have not attained equilibrium with the reservoir rocks.

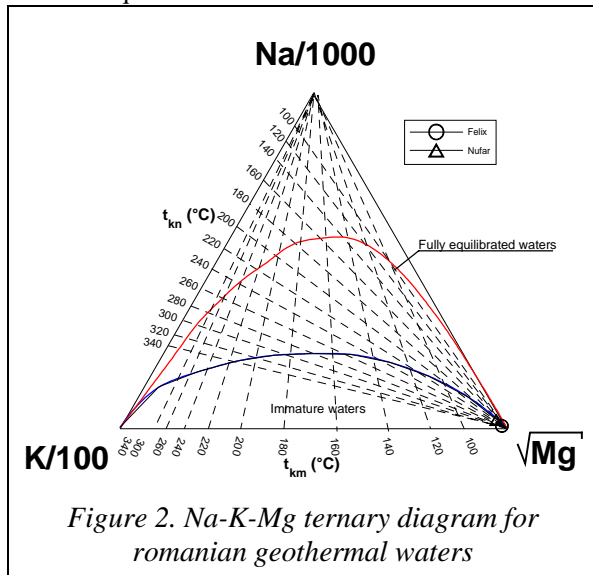


Figure 2. Na-K-Mg ternary diagram for Romanian geothermal waters

The water from Felix is classified as a calcium-bicarbonate water and the geothermal water from Nufăr is calcium-sulphate type.

GEOOTHERMOMETERS

The calculation of geothermal reservoir temperatures with the aid of chemical geothermometers involves various assumptions. Chemical geothermometry when applied to specific sites can be expected to reveal the temperature of the aquifer feeding the respective well. One of the basic assumptions is that a temperature-dependent equilibrium is attained in the geothermal reservoir between specific solutes and minerals. It is further assumed that the respective solutes are not affected by chemical reactions in the upflow where the cooling occurs. Several geothermometers have been developed to predict reservoir temperatures in geothermal systems.

The results of chemical analysis were used to calculate temperatures based on these geothermometers using the Watch aqueous speciation programme. The results of the geothermometry calculations are shown in Table 3.

Table 3. Geothermometry calculations

Well	Chemical geothermometers, °C		
	Quartz	Chalcedony	Na/K
Felix	66	33.8	316.8
Nufăr	93.3	62.2	167.4

The temperatures of the reservoirs indicated by the calculated chalcedony geothermometer are close to the production temperatures of the waters.

THE SILICA MIXING MODEL

The silica mixing model may be used to determine the source temperature of the hot water component.

The silica enthalpy mixing model was tried for the geothermal waters from Felix and Nufăr. It seems that there is no mixing of these waters with colder waters. The plots are located on the solubility curve of chalcedony (Figure 3).

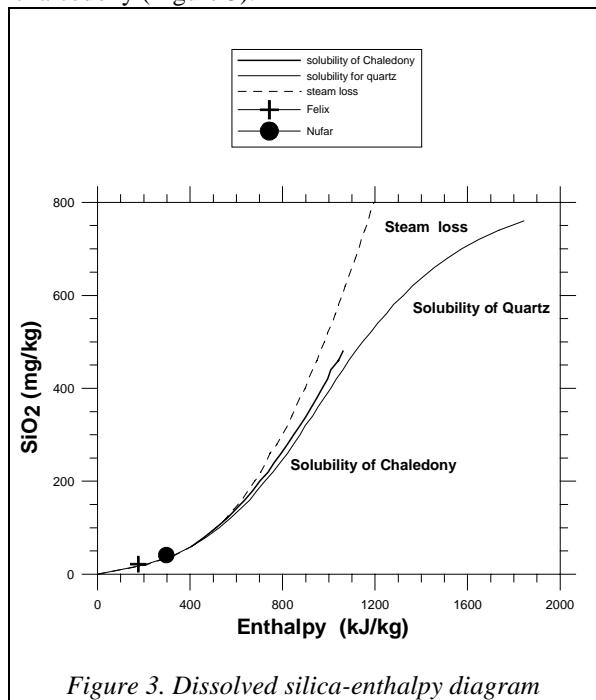


Figure 3. Dissolved silica-enthalpy diagram

PREDICTION OF DEPOSITIONS

The Watch program was used to model what happens in geothermal fluids under different conditions, first at reservoir temperature and then during water influx into the distribution system during production.

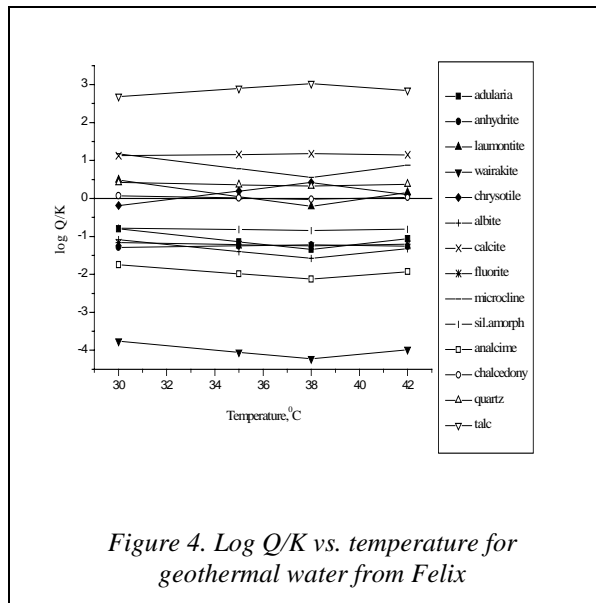
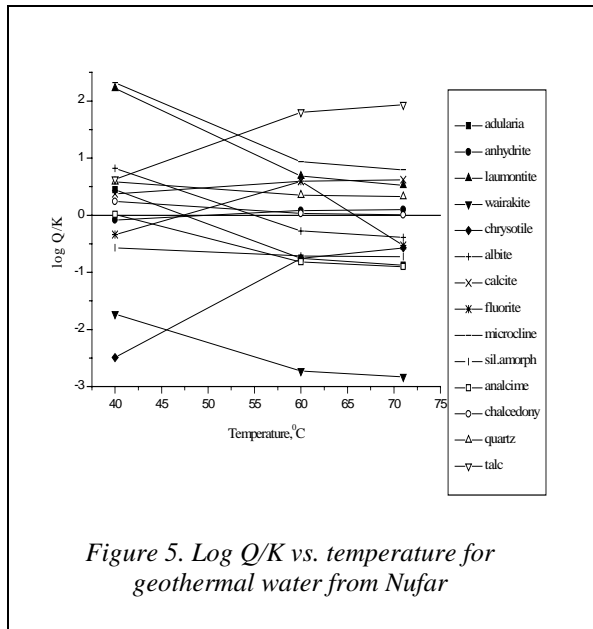


Figure 4. Log Q/K vs. temperature for geothermal water from Felix

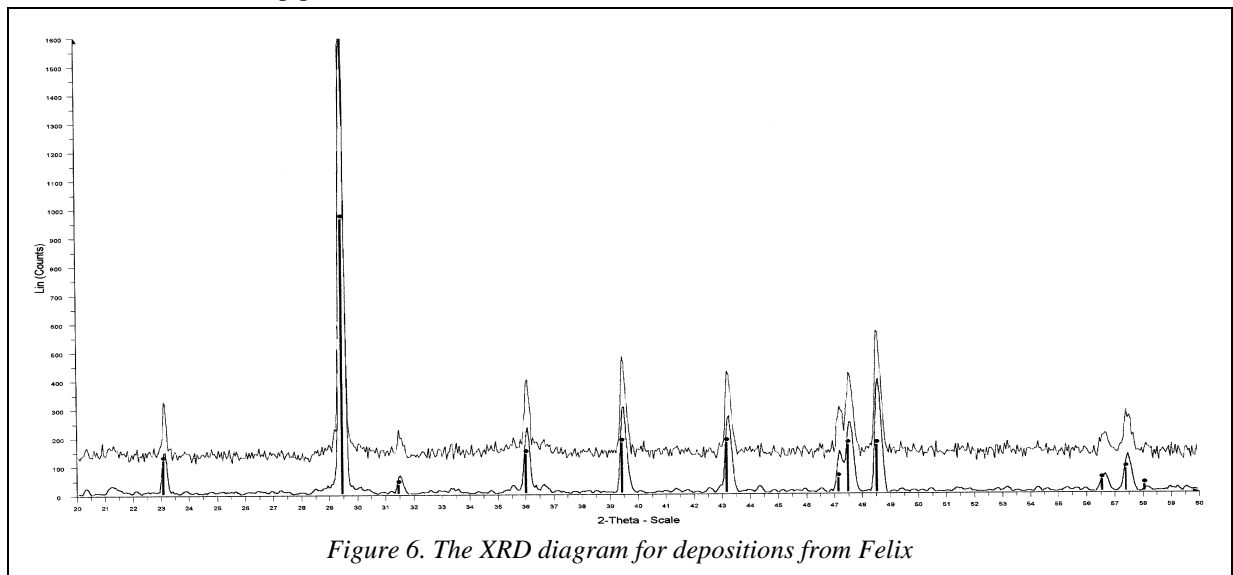
The diagram for Felix (Figure 4) indicates a supersaturation with calcite, talc, microcline and quartz at the wellhead temperature. There is an equilibrium with chalcedony at any temperatures which were used, assuming a conductive cooling during utilization. There is undersaturation in respect with the other minerals. Figure 5 shows a possible

scaling in respect with calcite at the wellhead temperature at Nufār. There is also a supersaturation with talc, microcline, laumontite. Anhydrite is close to the saturation line. There is an equilibrium with chalcedony. Most of the minerals tend to be fairly close to saturation at temperatures exceeding 60°C. Most of the lines intersect between 45 and 55°C. Minerals are in equilibrium at different temperatures in the interval mentioned before.



SOLID DEPOSITIONS FORMED DURING UTILIZATION

At Nufār there were not recorded scaling problems during geothermal water utilization. At Felix there were observed solid depositions in the distribution system during utilization. The scale was XRD analysed by using KαCu radiation. The sample consists of calcite as main. The amorphous phase has a high Fe content and for this reason it appears an elevated baseline on XRD diagram (Figure 6). This is due to the corrosion of the pipe.



The crystalline phase is formed by calcite, which is proved by the XRD analysis

CONCLUSIONS

The geothermal water from Felix is classified as a calcium-bicarbonate water and the geothermal water from Nufār as calcium-sulphate.

There is an equilibrium with chalcedony. There are no evidences of mixing of cold waters with hot waters in the reservoir.

The saturation index for calcite has a value more than 1 at Felix, which indicates scale for sure. The scale deposits from Felix are formed by calcite as a crystalline phase. At geothermal production well from Nufār the saturation index for calcite has a lower value. It might be scaling in the future.

It is recommendable to sample geothermal water at least two times a year. Based on good analytical results, thermodynamic data on different minerals, which could start to precipitate, could be obtained and to predict the scale potential before this problem occurs.

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