

Geochemical Evaluation of Fluids and Scales from Romanian Geothermal Production Wells of Bihor

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ABSTRACT

Chemical data interpretation is of major importance for maintaining a good production well. The credibility of the results of the laboratory analysis depends on the care taken in the collecting of samples and the analytical procedures adopted. The results of analysis of main elements in the water samples, the concentration of trace elements and nutrient components, as well as trace of heavy metals concentration in the water from the studied wells will be summarized for each well. For an initial classification, we will use diagrams calculated by the AqQa program. Then by using Giggenbach and Arnorsson triangular diagrams, we will have information regarding the water-rock equilibrium. The chemical geothermometers are the most important geochemical tool for exploration and development of geothermal resources. Geothermometers will be used to estimate subsurface temperatures, below the zone of cooling, expected to be encountered by drilling, using the chemical composition of wellhead waters. For geothermal wells where scaling problems have been recorded, metallic coupons will be installed into a laboratory set up, geothermal water from the well will be kept at a certain temperature for different periods and samples will be taken of the solid deposition. In order to do a chemical control of deposition and to find out the most efficient chemical additive, an experimental laboratory setup is installed, where geothermal water is running, first at wellhead temperature and later at a lower temperature, through a capillary tube. Depending on the type of scales occurring in the experiments, several additives will be selected. Also, the effect of different additive concentrations will be investigated. In order to determine the corrosion rates, the gravimetric method will be used, both in static conditions and in dynamic conditions.

1. INTRODUCTION

Through time, geothermal energy has been a very important resource of renewable energy, whose exploitation has an insignificant impact on the quality of the environment. Geochemical prospecting is one of the main tools to monitor its sustainable use. Collecting baseline data for monitoring the well and also to evaluate any impact on the environment caused by geothermal development is relevant for the local community. The hottest zone in Romania is situated in the western part of the country, in the Pannonian Basin.

Of the boreholes that have been drilled into the Oradea reservoir, one production well with economic importance in the area was chosen for this study: well no. 1717. The depth of this well is 2230 m. It had originally artesian flowrate from 15 to 20 l/s and recorded wellhead temperatures in the range of 70 to 90°C. It had been exploited with well no. 4767 on the Ioșia side of the town, for district heating and for swimming pools.

In the neighborhood of Oradea, at about 25 km to the south, well no.507 was selected for this research, which was drilled in Livada. The well appeared at first non-productive, but after acid stimulation the production went up to 8-12 l/s with a water temperature around 90°C at the wellhead. Since 1985 geothermal water from this well has been used for heating houses and to provide domestic tap water. In the last years the economic importance of this well has increased, with the geothermal water from well no.507 being used for greenhouse heating in Livada village.

2. CHEMICAL MONITORING OF GEOTHERMAL WATERS

Samples were taken for chemical analysis of the waters from wells 1717 and 507. Water sampling and treatment was according to best practice analytical procedures like developed by Icelanders, Pang and Ármannsson (2006), Kristmannsdóttir (2004), and Arnórsson, (2000).

Temperature and hydrogen sulphide were measured at the site. Hydrogen sulfide was measured in an alkaline solution by titration with mercury acetate with dithizone as indicator. The pH was measured using an electrometric method by a glass electrode combined with a reference potential inserted into the sample. Total carbonate was measured by alkalinity titration by 0.1 M HCl and backtitration by 0.1 M NaOH after flushing the carbon dioxide out of the acidified sample by nitrogen gas.

The following compounds: sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe) silica (SiO₂), and boron (B) were analyzed by ICP-AES methods. Chloride (Cl), sulfate (SO₄) and fluoride (F) were analyzed by ion chromatography. The analyzed trace elements were measured by ICP-MS techniques. The ones analyzed were aluminium (Al), lithium (Li), ammonia (NH₃), phosphate (PO₄), nitrate/nitrite (NO₃+NO₂), and heavy metals important for health and environmental issues (Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Zn).

The measured temperature of the water sample from well 1717 was 72°C, the pH was a basic one, 8.2 and the hydrogen sulphide concentration was 0.16 mg/L. At well 507, the water temperature at sampling was 86°C, the pH 7.95 and the H₂S concentration was 0.9 mg/L. Total dissolved solids are doubled for well 507 compared to the value of 460 mg/L from well 1717.

As demonstrated in the Schoeller and Durov classification diagrams, AqQa program (2005), (Figures 1 and 2), waters from the analyzed wells can be classified as calcium-sulfate for well 1717, and calcium-bicarbonate for well 507.

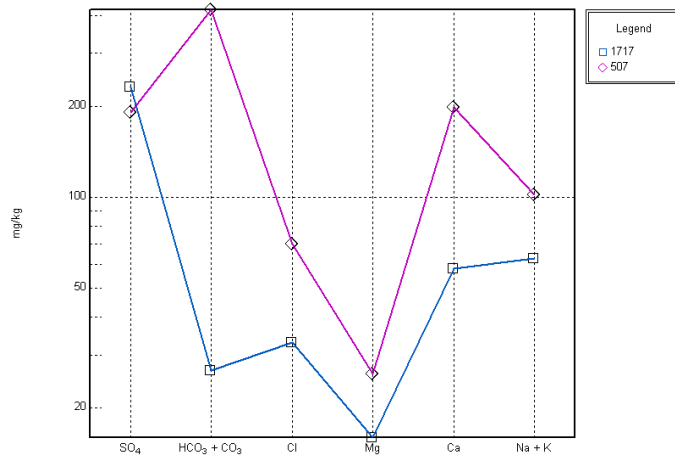


Figure 1: Schoeller diagram for the water samples.

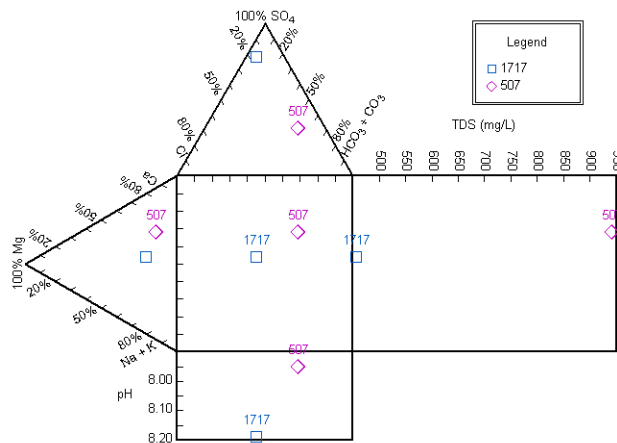


Figure 2: Durov diagram for classification of the water samples.

Considering the major anions, the Cl-SO₄-HCO₃ diagram illustrates the proportions of these anions presented in geothermal waters in the format of Giggenbach (1991). From Figure 3 you can notice that waters from well 507 are located within regions of high bicarbonate concentration and can be classified as peripheral waters, while waters from well 1717 are steam heated waters, close to the sulphate corner.

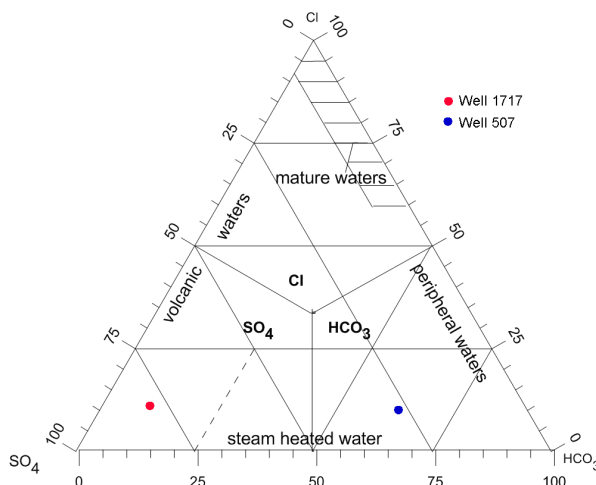


Figure 3: Classification of water samples based on the Cl-SO₄-HCO₃ ternary diagram.

The results of analysis of trace components in the water samples are summarized in Table 1.

Table 1. Results of minor concentration compounds

Well no./ conc.	PO ₄ mg/L	NO ₃ +NO ₂ mg/L	NH ₃ mg/L	Li mg/L	Al mg/L	Ba μg/L	Cd μg/L	Co μg/L	Fe mg/L
1717	<0.04	<0.06	0.104	0.091	1.86	75	<0.02	<0.02	0.038
507	<0.04	<0.06	0.641	0.3	3.99	158	<0.02	<0.02	0.86
Admissible limits	0.5	0.3	0.5	30	0.2	700	3	<0.02	0.3
Well no./ conc.	Cr μg/L	Cu μg/L	Mn μg/L	Mo μg/L	Ni μg/L	Pb μg/L	Zn μg/L	B mg/L	F mg/L
1717	2.69	<0.2	45.1	2.72	<0.2	0.41	3.57	0.223	0.9
507	2.90	0.28	15.4	<0.3	0.65	0.47	5.62	1.65	2
Admissible limits	50	100	300	20	20	10	3000	5	5

Apart from the ecological impact of using geothermal water from this well, from Table 1 it seems that the discharge would not be of any concern for health and environment (Mănescu et al., 1981).

The plot for the selected wells data is presented in the Na-K-Mg ternary diagram of Giggenbach (1991) and Arnórsson et al. (1983) (Figure 4). The figure shows that these waters do not reach the fully equilibrated water curve. They have a high percentage of Mg, so they lie in the immature region. Since this implies that these waters have not attained equilibrium with the reservoir rocks, it would be inaccurate to use them for Na/K geothermometer calculations.

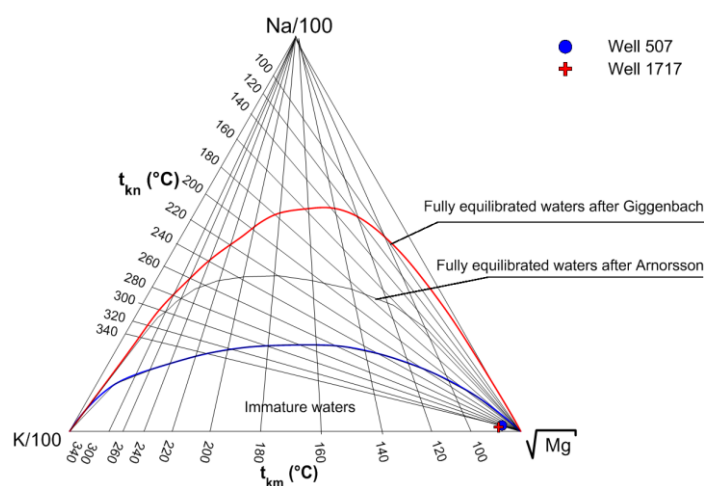


Figure 4: Na-K-Mg equilibrium diagram.

It is of relevant importance to monitor any change in the reservoir temperature during well exploitation in order to use it in an efficient way. Temperature, time and fluid composition all affect different crystalline forms of silica. Therefore, for waters being in contact with rocks at a given temperature, in some places, quartz or chalcedony may control dissolved silica. The chalcedony geothermometer is based on the solubility of chalcedony. In the range of 0-250°C, on the condition of no steam loss, the chalcedony geothermometer or quartz geothermometer could be applied. Cation geothermometers, like the Na-K geothermometer, are based on the temperature dependence of ion exchange or partitioning of alkalis between solutions and solid phases.

Estimation of reservoir temperature was done using the speciation program WATCH (Arnórsson and Bjarnason, 2004). The program used the functions for quartz, chalcedony and Na/K ratio geothermometers, and the results are summarized in Table 2.

Table 2. Geothermometry calculations

Well no.	Wellhead temperatures, °C	Chemical geothermometers, °C		
		Quartz	Chalcedony	Na/K
1717	72	-	-	347.2
507	86	112.7	83.3	280.8

The temperature of the reservoir indicated by the calculated chalcedony geothermometer is very close to the production temperature of the water from well 507. Unfortunately, for well 1717, due to the very low silica concentration (2.4 mg/L) in the sampled geothermal water it was not possible to apply the silica geothermometers.

The Mixing model (Truesdell and Fournier, 1977), which allows the estimation of a hot water component in mixed waters in springs or discharge from shallow drill holes, was applied for well 507. The model used the silica content of the geothermal water sample (65 mg/L) and the enthalpy of the water; the result for the temperature of the deep hot water was 108°C (Figure 5).

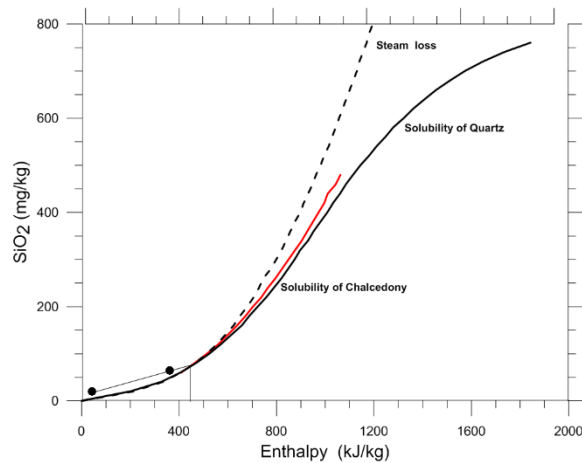


Figure 5: Dissolved silica-enthalpy diagram.

3. MONITORING THE SCALES FORMED DUE TO MINERAL DEPOSITS AND CORROSION PRODUCTS

The study of fluid-mineral equilibria is a very useful tool in that it provides practical applications for the assessment of equilibrium/disequilibrium conditions for geothermal fluids, on which almost all the reservoir processes depend. Such applications are useful in prediction of scaling and corrosion tendencies in a particular geothermal system. In this paper, the simulation computer program WATCH (Arnórsson and Bjarnason, 2004) (Figure 6, Figure 8), was used to calculate the saturation indices for particular mineral phases believed to occur in the reservoirs.

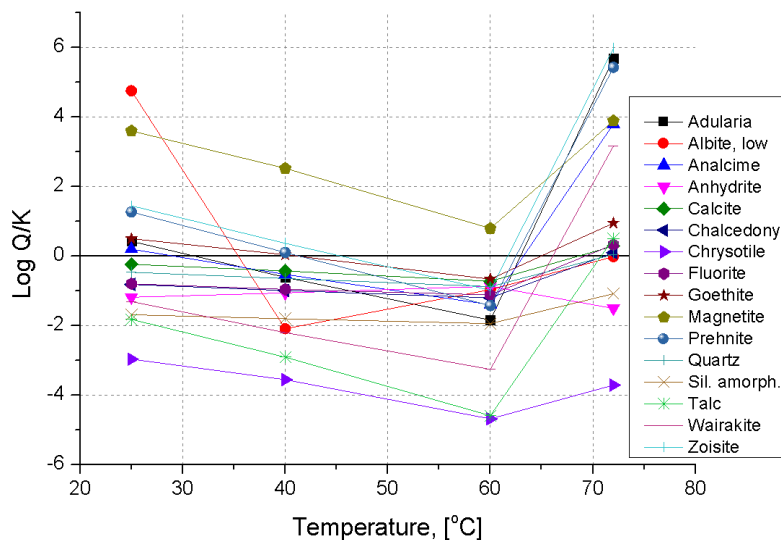


Figure 6: Log Q/K vs. temperature for selected water from well 1717.

At well 1717 magnetite products were assessed at the wellhead temperature and also at lower temperatures, which are reached after utilization. For this reason, studies were performed on corrosion rates of the coupons inserted in the flow of geothermal water. In order to determine the corrosion rates, in the present paper gravimetric method was used, both in static conditions and in dynamic conditions. Corrosion tests were conducted using carbon steel coupons, like the pipe material exposed to fluids from 1717 well. The coupons were weighed to 0.001 g accuracy before introducing them into the test. The water bath was kept at constant temperature of 45°C. The measurements were done periodically within almost two months. Changes in weight after immersion in the geothermal water were used to determine the effects of corrosion for each coupon. The results are shown in Figure 7.

The data from Figure 7 indicate that the strongest corrosion process of the coupons occurring in geothermal water from well 1717 was during the first month of testing. Then, the corrosion process decreased in time, being almost stable in the last two weeks, which happened probably due to corrosion products with a passive action, forming on the coupons surface. As type of corrosion phenomenon, a uniform corrosion was followed by a pitting corrosion. The measurements done at a temperature maintained at the wellhead temperature indicated in the beginning of the experiments a corrosion rate about two times higher in dynamic conditions compared to static ones.

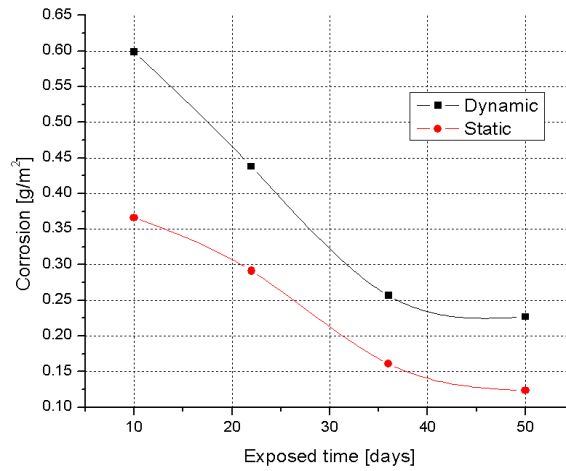


Figure 7: Changes of corrosion rate in time, well 1717.

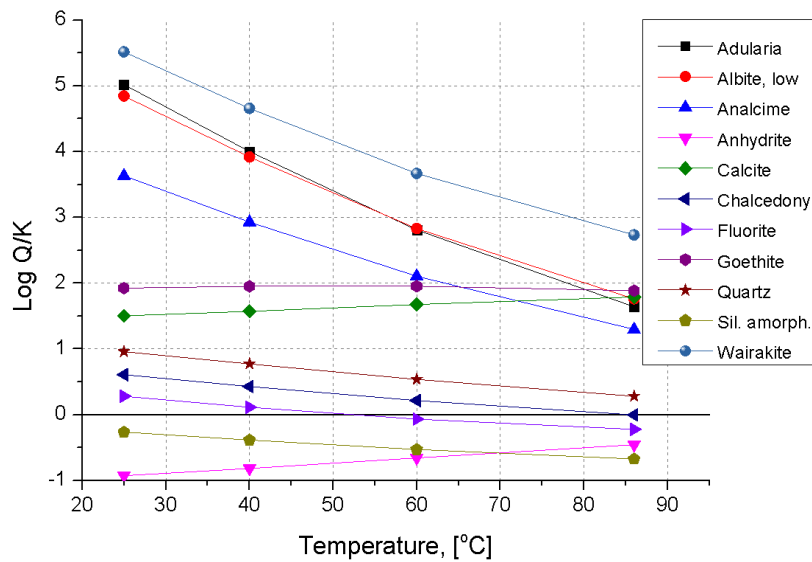


Figure 8: Log Q/K vs. temperature for selected water from well 507.

At Livada well 507, supersaturation of calcite was recorded, starting at wellhead temperatures and being assessed at lower temperatures as well. A laboratory technology for monitoring of scales was developed. Geothermal water from well 507 was pumped at constant flowrate through a stainless steel capillary tube immersed in a water bath at 86°C. In order to test the efficiency of additives on calcium carbonate scale, we tried two types of additives, a polyphosphate and a polyacrilate. We started with a dosage of 15 mg/L. In the next runs we tried lower concentrations, in order to settle the lowest dosage needed to avoid calcium carbonate precipitation. Selected experimental data are presented in Figure 9. Both additives are useful in chemical treatment for calcium carbonate scales, reducing the deposit formation by adding a relatively low concentration. The best efficiency was obtained with polyacrilate.

4. CONCLUSIONS

A change in the chemical composition of the geothermal water will often precede cooling in the field and data obtained by chemical monitoring of the fluids may give a warning in time for preventive action. Two important production wells from Bihor county were investigated in this study. Geothermal waters were sampled for analysis using standard methods. The results of the laboratory analysis allowed a classification of these waters. The dominating cation is calcium for both wells, whereas the dominating anion is sulphate, respectively bicarbonate. The mineralisation is higher in the water from well 507. There we also detected trace components. Within these, the content of heavy metals is in the limits not dangerously for people and environment. The hydrogen sulphide content may contribute to accelerating of the corrosion process of the equipment.

The temperature of the reservoir was calculated by silica geothermometers for well 507. The result was a deep water temperature a little higher than the wellhead temperature, meaning that a cold water from the upper layers may mix with the hot groundwater.

Based on the chemical geothermal water composition, we assessed the minerals possible to precipitate from the water. For well 507 formation of calcite was found. Laboratory test confirm calcium carbonate precipitation without any treatment with chemical additive and, after applying chemical treatment, the best efficiency was obtained with the polyacrilate additive.

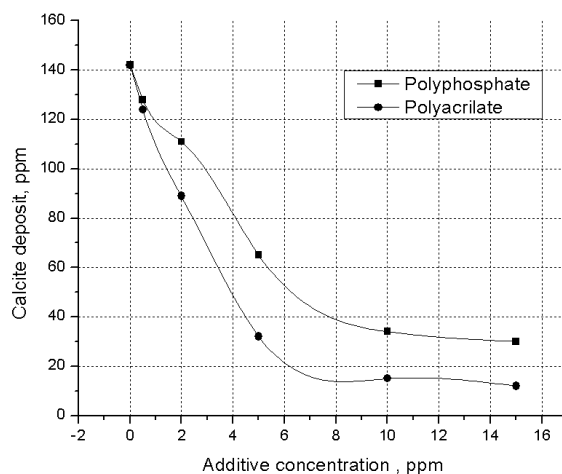


Figure 9: Additive efficiency in deposition control.

For well 1717, the simulation program indicated formation of magnetite, which means we can expect corrosion processes during geothermal water utilization. Laboratory experiments confirmed the assessed problem.

By increasing the analyzed compounds into the geothermal water as close to the real situation as possible, the programs are likely to succeed to give the exact mineral products of precipitation and /or corrosion, calculated both at the wellhead temperature and at lower temperatures due to geothermal water utilization.

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REFERENCES

- Kristmannsdóttir, H.: Sampling of hot and cold water for geochemical measurements Instructions for practicals in the course VAG1103 Háskólinn á Akureyri, Auðlindadeild, Skýrsla HK- 04/10, 11 s, (2004).
- Pang, Z. and Ármannsson, H.: Analytical procedures and quality assurance for geothermal water chemistry. The United Nations University Geothermal Training Programme, Orkustofnun, Reykjavik, 172p., (2006).
- Arnórsson, S. (ed.): Isotopic and Chemical techniques in Geothermal Exploration, Development and Use. International Energy Agency Vienna, (2000).
- AqQa, Spreadsheet for water analyses, RockWare, Golden, (2005).
- Giggenbach, W.F.: Chemical techniques in geothermal exploration. In D'Amore, F. (coordinator), *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, (1991), 119-142.
- Mănescu, S., Dumitrache, S., Cucu, M., Fuiuogă E.: Igienea mediului, Editura Medicală București, (1981), 81-118.
- Truesdell, A.H. and Fournier, R.O.: Procedure for estimating the temperature of a hot water component in a mixed water using a plot of dissolved silica vs. enthalpy, *U.S. Geol. Survey J. Res.*, **5**, (1977), 49-52.
- Arnórsson, S. and Bjarnason J.Ö.: Icelandic Water Chemistry Group, *The chemical speciation programme WATCH*, version 2.3. Science Institute, University of Iceland, Orkustofnun, Reykjavik, (2004).