Characterization and Geochemical Constraints on Formation Conditions in a Low-Temperature Geothermal Field

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Abstract: A low temperature geothermal field is located in the north western part of the country. Scaling encountered in exploitation equipments yield to a decrease in the production efficiency, being a major problem at geothermal water utilization. The objectives of this work are to chemically characterize scales formed as a result of mixing of waters from different aquifers, to define the geochemical constraints and the formation mechanisms of the scales and to model those with the aid of geochemical speciation and reaction path programs. Scales, formed in surface pipelines have been characterized by chemical analysis, X-ray diffraction and thermo-differential analysis. With the aid of computer program for geochemical aqueous speciation, the geochemical constraints of the formation of scales were modeled. The experimental results obtained by analysing on scales were compared to those obtained by the use of simulation program. In order to minimize scaling, tests in static conditions have been conducted.

Keywords: geothermal field utilization, scales, simulation program

1. Introduction

The aim of this study was to appreciate the need for chemical monitoring and predict possible scaling during production in a Romanian geothermal field. The field chosen for this study is the Bors reservoir. It is situated in the Western Plain of Romania, about 6 km northwest of the town of Oradea. Bors is a closed aquifer with a small surface area of 12 km^2. It is located in fractured Triassic limestones and dolomites.

The production wells from Bors were used to provide base load and for the heating of 6 hectares of greenhouses.

2. Materials and methods

The analytical methods used for geothermal water analysis [1] are noted in Table 1. The analytical procedures for depositions analysis are briefly described in Table 2

TABLE 1. Analytical methods used for the constituents determined from water

Constituent	Method	Brief description
pH	Electrometric	A glass electrode in combination with a reference electrode is inserted into the sample and pH and temperature values recorded.
CO_2	Electrometric titration	After the pH sample was adjusted to 8.2 it was titrated with HCl to pH=3.8.
Na, K	Flamephotometry	λ=589 nm, respectively 767 nm.
Ca, Mg	Titration	By using EDTA at pH=12-13 for calcium in presence of murexid as indicator and at pH=10 for $Ca^{2+}+Mg^{2+}$ in presence of eriochrom, magnesium resulting by difference.
Fe	Spectrophotometry	It was used the method with o-phenantroline, the absorption was read at 510 nm.
B	Spectrophotometry	Azomethine H/ ascorbic reagent added, absorption was read at 420 nm.
SiO_2	Spectrophotometry	At pH=1-1.5 a silico-molibdate complex is formed, absorption was read at 410 nm.
Cl	Titration	Mohr method, by using K_2CrO_4 as indicator.
SO_4	Titration	The sample was titrated with $Ba(ClO_4)_2$ by using thorin as indicator.
TDS	Gravimetric	Sample was evaporated and dried at 105°C

The solid samples were also structural analysed:
- thermogravimetric by the use of a Derivatograph Q-1500D; the sample was grounded very fine and it was heated up to 1000°C with a heating rate of 10° / minute;

- by X-Ray diffraction; the diffraction patterns have been registered with a PHILIPS PW 1400 X-ray spectrometer with Kα Cu radiations.

TABLE 2. Analytical methods used for deposition sample

Component	Methodology
CaO	Complexonometric determination
MgO	Complexonometric determination
Fe_2O_3	Titration with potassium bichromate, by using phenilantranilic acid as indicator
loss	Calcination at 1000°C

3. Results and discussions

As chemical changes will often precede changes in temperature and pressure, it is recommended to monitor the chemical composition of the fluids in a geothermal system

Selected data on the chemical composition of geothermal waters from a production well from Bors are presented in Table 3. The wellhead temperature measured during collection of water samples was 90°C.

TABLE 3. Chemical composition of geothermal waters from Bors geothermal field, in mg/l

pH	CO_2	SiO_2	B	Na	K
7	1068	127	49	4230	385
Ca	Mg	Fe	Cl	SO4	TDS
122	13.2	9.6	6320	115	11210

The data presented have the ionic balance within admissible limits, not exceeding 5%. Taking into account the data from Table 3 you can notice the high values of carbon dioxide, the dominant anion is chloride and sodium concentration is high as well. In these rather saline waters the dissolved solids exceeds 10 g/L.

An assessment of potential scaling problems can be obtained through interpretation of the analytical data. Using the Watch simulation program [2], the log solubility indexes for different minerals were calculated. A positive value for the relative log solubility of a mineral means that the solution is supersaturated with respect to that particular mineral and theoretically it could start to precipitate.

The analysis from the well from Bors have been calculated in the Watch program at production temperature and by cooling in steps of about 30°C, temperatures which can be reached during and after geothermal water utilization (Figure 1). At the measured temperature, 90°C, is much closer to the chalcedony equilibrium temperature [3]. Wollastonite, chrysotile, anhydrite, and amorphous silica are undersaturated. When the temperature of the geothermal water decreases, the minerals calcite, quartz are still supersaturated, while talc becomes undersaturated.

Scaling reduced wells productivity, their performance and efficiency. Major problems have arisen in the heating service from Bors due to deposition processes. After the production at Bors was stopped, the pipes from the wells were removed and deposition samples were taken for chemical and structural analysis.
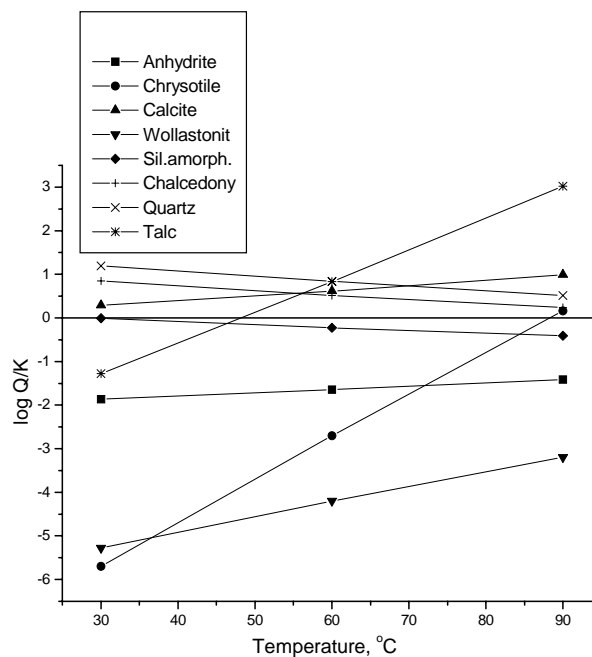

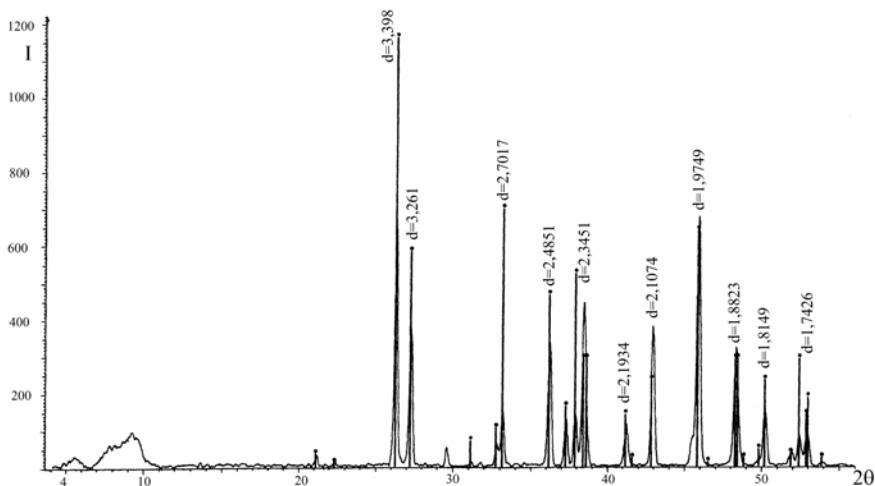Figure 1. Mineral equilibrium diagrams for the thermal waters in research area

In order to determine the composition of solid samples, first, quantitative analysis were made. The solid samples were desintegrated and then calcium, magnesium [4] aluminium and ferrum were volumetric determined. The chemical results are shown in Table 4. Data from Table 4 demonstrated that calcium is the main element of solid depositions from Bors. That could mean that calcium carbonate scale is the primary problem.

The solid samples were also structural analysed. The XRD diagram (Figure 2) obtained for the solid depositions shows there are aragonite crystals in the sample.

TABLE 4. Chemical composition of solid deposition from Bors, in %.

CaO	MgO	Fe_2O_3	Calcined loss
54.4	1.1	0.7	42.7

From the thermo-gravimetric diagram (Figure 3) you can notice a decomposition process that starts slowly at about 650°C and reaches a maximum at 930°C. The mass loss is about 43.2% in the range of temperatures 650-1000°C. This means that the deposition sample consists primarily of calcium carbonate, the loss being carbon dioxide. In conclusion, taking into account the other kind of analyses made, the solid deposition consists of calcium carbonate as aragonite crystalline form and traces of iron oxide due to corrosion of the pipe. The presence of Mg in depositions could be a result of precipitation from geothermal water.

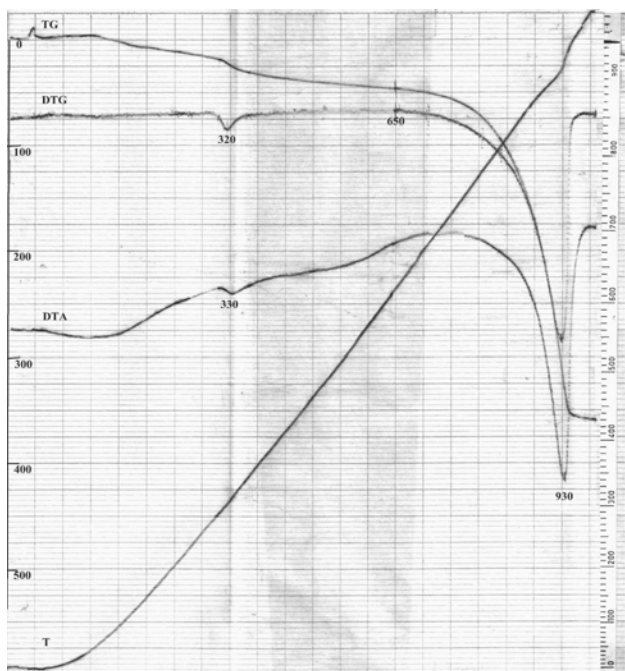Figur 2. The XRD diagram for depositions.

Figure 3. The thermogravimetric diagram

bath at 90°C. Different concentrations of the additive were used to generate the performance profile. The experimental results are shown in Figure 4. In static conditions the used additive can prevent the separation of calcium carbonate from waters at a minimum dosage of 6 mg/l.
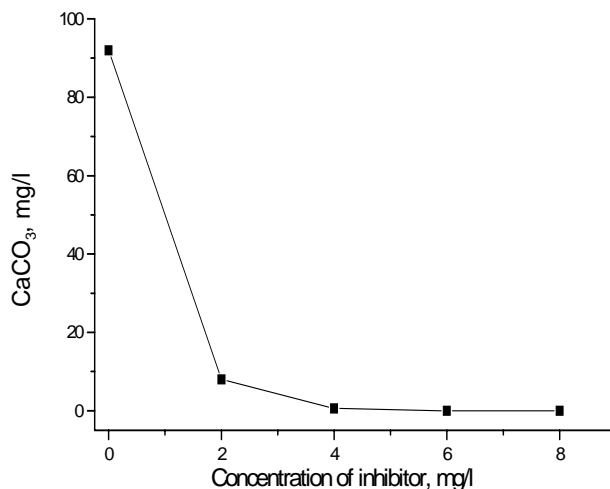

Figure 4. Calcium carbonate deposition control

Calcium carbonate was found out the major scale formed up to the studied low temperature geothermal well. To control this scaling problem, an acid treatment, an additive treatment or a mechanical cleaning may be employed [5]. The first method has a number of drawbacks. Due to these, the second method must be more practical

In order to measure the ability of additives to control calcium carbonate deposition, a laboratory test was made. Geothermal water from well, containing 122 mg Ca^{2+}/l was placed in a water bath at 90°C for duration of one hour. From this water calcium carbonate was separated. Ammonium salt of the copolimer of vinil acetate with maleic anhydride additive was introduced into the water

4. Conclusions

Monitoring the chemical properties of geothermal fluids has proved to be an important tool in the management of geothermal production in low temperature geothermal field as Bors. The results have been used to forecast any changes in production characteristics. The simulation program showed that there might be danger of scaling, so monitoring is required.

In order to evaluate the solid samples removed from equipments a complete analysis was made. Calcium

carbonate is substantially deposited in wellhead pipe. The chemical and structural results of the solid depositions confirmed the predictions given by the simulation program. Being better to prevent scale formation before it occurs, the use of simulation programs which could predict possible scaling under differing conditions of utilization geothermal fluids should be considered by system operators. An easy test by which calcium carbonate deposition is controlled by additives was presented for static conditions, but it can be extended for geothermal operation, without substantial costs.

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