GEOCHEMICAL STUDIES ON A LOW-TEMPERATURE GEOTHERMAL WELL

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ABSTRACT

This paper presents the results from a study of the composition of waters and the structure of depositions formed by direct heating utilization of geothermal waters. First, the chemical composition of geothermal waters from a selected low-temperature well was determined by standard methods. The silica enthalpy mixing model was used to find out the source temperature of the hot water component. The water – minerals equilibrium was studied by using a simulation program. The scales formed due to corrosion and deposition, during geothermal water utilization, were XRD analysed in order to identify them. The corrosion resistance of carbon steel was estimated using gravimetric and electrochemical methods as: chronopotentiometry and polarization curves, at the temperatures of 20°C, respectively 80°C, in static and dynamic conditions.

INTRODUCTION

One of the boreholes that have been drilled into the Oradea reservoir used as production well is well 4796. This well was drilled in 1981. At the completion of drilling appeared to be low productive, the well yielded less than 3 l/s. The productivity of the well increased to about 16 l/s by acid stimulation. Geothermal water from this well has been supplying the heating system for the University of Oradea. The average wellhead temperature is 80°C.

Once the University developed, the necessity of an energy resource for direct heating has increased. In order to solve this problem it was fixed a submersible pump, that gave good results, obtaining a flowrate of more than 50 l/s. Due to the economical importance of well 4796 a continue monitoring of the chemical characteristics of this low-temperature geothermal well is welcomed.

WATER CHEMICAL CHARACTERISTICS

To determine the major elements of the geothermal water from well 4796, specific analyzing methods were done, the chemical results being summarized in

Table 1. The chemical characteristics indicate a sulphated-calcium-bicarbonated water.

Table 1. Chemical composition of geothermal waters, in mg/l.

Component	Well 4696
pH	6.5
CO_2	208
B	25.2
SiO_2	49
Na	39
K	7.1
Mg	34
Ca	275
Cl	20.6
SO_4	664
Fe	0.5
TDS	1140

ASSESSMENT OF RESERVOIR TEMPERATURE

The results of chemical analysis of geothermal water were used to calculate temperatures based on geothermometers, using the Watch aqueous speciation programme. The results of the geothermometry calculations are shown in Table 2.

Table 2. Geothermometry calculations, in °C.

Wellhead temp.	Chemical geothermometers		
	Quartz	Chalcedony	Na/K
82	101.2	70.8	264.7

The temperature of the reservoir indicated by the calculated chalcedony geothermometer is close to the production temperature of the water.

The dissolved silica concentration of a mixed water may be used to determine the temperature of the hot water component. The silica mixing model uses a plot of dissolved silica vs. the enthalpy of liquid water. It was tried for the geothermal waters from well 4796. The plots are located on the solubility curve of chalcedony (Figure 1). The deep water temperature by mixing model is 91°C.
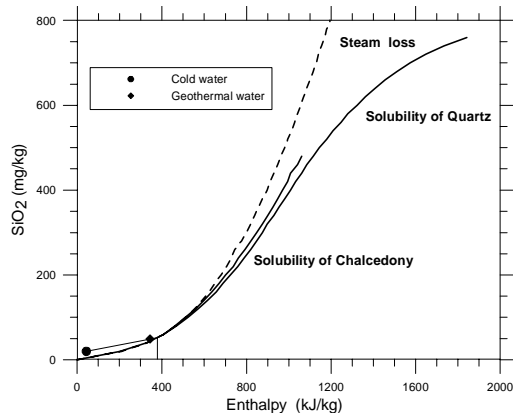
Figure 1. Dissolved silica-enthalpy diagram.

STUDIES ON DEPOSITIONS

To predict the potential danger of scaling and corrosion, the Watch program computes the chemical composition of geothermal water at the wellhead temperature and then at lower temperatures reached by water utilization and provides the values of the activity products for mineral dissolution reactions.
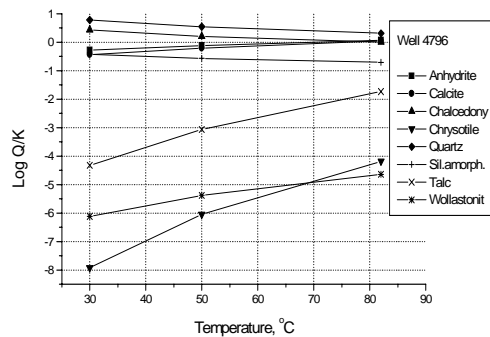

Figure 2. Saturation indexes for different minerals vs. temperature

As we can see in Figure 2, in well 4796, a potential scaling can be expected as the log Q/K for quartz, anhydrite and calcite have positive values.

At well 4796 there were observed solid depositions in a heat exchanger, when it was removed. A sample of depositions was taken for analysis by X-ray diffraction.

The sample was identified using a Philips PW1710 diffractometer employing a Ni-filtered Cu k-alfa radiation at 40 kV and 20 mA with 1° devergence and receiving slits. The raw data was handled using an EVA software from BrukerAXS. Patterns were evaluated and compared using the Powder Diffraction File PDF-2 Database Sets 1-46 from International Centre for Diffraction Data.

The crystalline phase (Figure 3) is formed by quartz and calcite. The crystal structure of the carbonate indicates that there might be some other cations in the framework, possibly magnesium, but it is carbonate anyway, mostly with calcium.

CORROSION STUDIES OF CARBON STEEL IN GEOTHERMAL WATER

The studies were based on the anodic and cathodic polarization curves of carbon steel, in geothermal water from well 4796, in potentiostatic conditions at 20°C, gravimetric determination of the corrosion rate and potential – time evolution.

For the polarization curves in potentiostatic conditions, a potentiostat and a compartmented electrochemical cell have been used (Figure 4), using 20 mV/min step. The working electrode had a geometrical area of 1,03 cm^2 and was mechanical prepared by polishing with different types of abrasive paper, till a glossy surface was obtained. The electrode was degreased with sodium carbonate, washed with distilled water and electrochemical treated in the polarization cell, at –800 mV$_{SCE}$ for 5 minutes. The auxiliary electrode was a platinum plate, with 2 cm^2 area, and a saturated calomel electrode (SCE) was used as reference electrode.
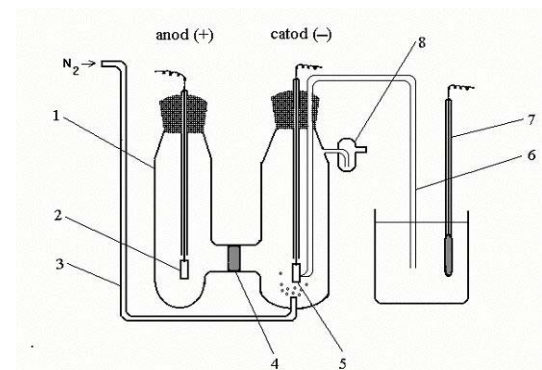

Figure 4. Electrochemical cell for polarization curves in potentiostatic conditions. 1-separate electrodic cell, 2-auxiliary electrode, 3-tube with N_2, 4-porous frit, 5- working electrode, 6-Luggin capillary, 7-reference electrode, 8- hydraulic closing.

In Figure 5 are presented the anodic and cathodic polarization curves of 37 carbon steel in geothermal water, at 20 °C, in the presence of oxygen.

The potential in open circuit, which attained a steady value after 10 minutes of cathodic treatment, was considered the corrosion potential of the metal. From this value, the working electrode was polarized, first in cathodic direction, and in the second experiment in anodic direction.
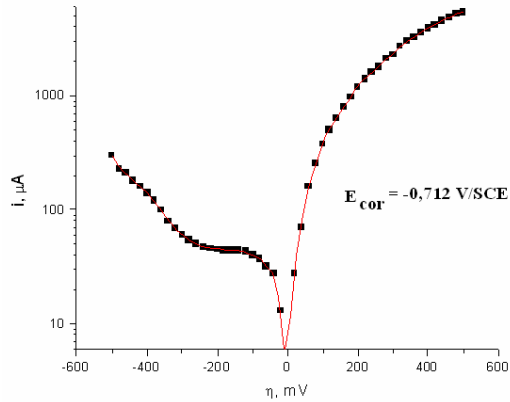
Figure 5. Potentiostatic polarization curves (20mV/min step) for carbon steel in geothermal water at 20°C.

As it is shown in Figure 5, the cathodic reaction is diffusion controlled, which it was expected, taking into account that the reduction of dissolved oxygen was the only thermodynamic possible reaction. In these conditions, the corrosion rate of the steel will be described by the limited current of oxygen reduction:

$$v_{cor} = K \cdot i_{cor} \qquad (1)$$

where: v_{cor} - corrosion rate $(g/m^2 h)$, K-electrochemical equivalent of iron (1.044 g/Ah), i_{cor} - corrosion current density, equal with the density of limited current of oxygen reduction: i_D=42,71 $\mu A/cm^2$ (the working electrode surface was 1,03 cm^2 and the limited current density 44μA).

The value of the limited diffusion current density, i_D, in A/cm^2 is comparable with the calculated value using the next relation (2):

$$i_{D_{O_2}} = \frac{z \cdot F \cdot D_{O_2}}{\delta} \cdot c_{O_2} = 40.84 \cdot 10^{-6} \qquad (2)$$

where: z = 4, the number of transferred electrons at the reduction of one mole of oxygen, D_{O_2} = diffusion coefficient of oxygen in water at 20°C, δ = medium value of the diffusion layer growth for static electrolytes, c_{O_2} = concentration of dissolved oxygen calculated from the gas laws, in mol/cm^3:

$$c_{O_2} = \frac{6.36 \cdot 273}{1000 \cdot 22400 \cdot 293} = 0.02645 \cdot 10^{-5} \qquad (3)$$

Because the solubility of oxygen decreases with the rising temperature the corrosion rate is expected to decrease in the same way. In Table 3 are presented the solubilities of oxygen in air saturated water at the pressure of 1 at., the limited current densities, the corrosion rates, and the penetration coefficients at different temperatures.

Table 3. Solubilities of oxygen in air saturated water at the pressure of 1 at., the limited current densities, the corrosion rates, and the penetration coefficients at different temperatures.

t, °C	20	40	60	80
O_2 cm^3	6.36	4.71	3.25	2.0
$c_{O2} \times 10^5$ mol/cm^3	0.02645	0.01833	0.0120	0.00696
$^1 D_{O_2} \times 10^6$ A/cm^2	40.84	28.30	18.53	10.75
v_{cor}, $g/m^2 h$	0.4264	0.2954	0.1935	0.1122
P, mm/year	0.4734	0.3282	0.2150	0.1247

The calculated corrosion rates, from Table 3 in according with the corrosion resistance of metals indicate the studied carbon steel to be in a relative steady state in the air saturated geothermal water at atmospheric pressure, till 80°C and in a steady state at higher temperatures. If the access of oxygen in the water is avoided, it might be expected an increasing of the corrosion resistance.

The gravimetric measurements were performed in static and dynamic conditions, at 80°C. In static conditions 3 carbon steel samples were parallel exposed in Berzelius covered glasses, and maintained 12 hours at constant temperature of 80ºC, respectively 20ºC. In dynamic conditions, 4 samples were parallel exposed in a glass cell, which also permitted the measuring of the corrosion potential in time variation (Figure 6). The cell was connected to a thermostat, used to maintain the temperature at a constant value and to circulate the water with a rate of 0.6 L/min, 12 hours per day. The other experiments were performed at 20ºC, in static conditions. The corrosion products were removed from the exposed samples using an ammonium citrate solution (10%) and ammonia, followed by washing with water and acetone.
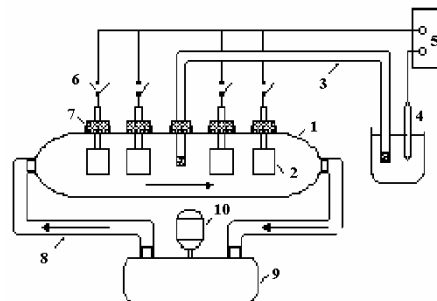

Figure 6. Installation scheme used for the gravimetric determinations and for the measuring of the potential-time variation in dynamic conditions

In figure 6 there were used the following notations:
1-glass cell, 2-samples, 3- electrolytic siphon (salt punt), 4- calomel saturated electrode, 5- electronic voltmeter, 6-switcher, 7-rubber bung, 8-rubber tube, 9-thermostat, 10- electric engine.

The gravimetric determination of the corrosion rates were made for different times of exposure: 1, 7, 14 and 21 days, in geothermal water, at 80ºC, in static and dynamic conditions. In the same time the corrosion potentials were measured. The results of these experiments are shown in Table 4 and Figure 7.

Table 4. Corrosion of carbon steel in geothermal water at 80°C

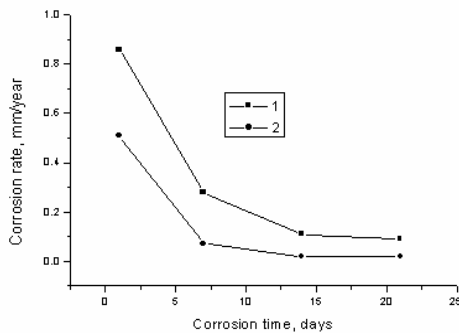| Time [days]	1	7	14	21
Static conditions				
v_{cor} [g/m^{2}h]	0.4545	0.0648	0.0176	0.0153
P [mm/year]	0.5050	0.0720	0.0196	0.0170
E_{cor} [V$_{SCE}$]	-0.722	-0.705	-0.690	-0.684
Dynamic conditions				
v_{cor} [g/m^{2}h]	0.7717	0.2498	0.0944	0.0821
P [mm/year]	0.8574	0.2776	0.1049	0.0912
E_{cor} V$_{SCE}$	-0.736	-0.722	-0.701	-0.695

Figure 7. Changes of corrosion rate of carbon steel with the exposure time in geothermal water, at 80°C in different conditions: 1-dynamic, 2-static

The corrosion rate of carbon steel decreases with the time and after 14 days of exposure it becomes stable at values which describe the metal as relative corrosion resistant. This decreasing of the corrosion rate is determined by the covering of the samples with crusts and corrosion products, which are consolidated in time.

The corrosion potentials easily shift by time to less negative values, because of the accumulation of the corrosion products on the metal surface, which remains still active. In dynamic conditions, the potentials shift to more negative values than in static conditions. This behavior might be determined by the limiting concentration of oxygen in dynamic condition, taking into account that the experiment was performed in a closed system and it was not any access of oxygen.

Maintaining the corrosion potentials at active values during the experiment is determined by the cumulating effect of both high temperature and the presence of the chloride ions. If we compare the results of the gravimetric determinations with the calculated ones from the limited current of oxygen reduction, it is obvious that the first are giving semnificatively higher corrosion rates, which means that the corrosion process is much complex and sensitive to the periodic variation of the temperature from 80°C to room temperature and the reverse, and also to the electrolyte circulation.

It may be underlined that the experimental results permitted the evaluation of the carbon steel resistance only at general corrosion. It is well known that the presence of the chloride ions, in case that the metal surface is covered by passivation films (thermic equipments), could produce a concentrated attack (pitting) on the surface if there are discontinuities of the passive film.

In lab conditions, the localized attack wasn't noticed because the exposure times were relative short and the samples surface were uniform prepared before the experiments, which means different conditions comparing with a thermic equipment.

CONCLUSIONS

The geothermal waters from the studied well can be characterizied as sulphated-calcium-bicarbonated waters.

The chemical composition of geothermal waters from well 4796 from Romania were interpreted by using the Watch program, which gives information about the mineral equilibrium and a basis to assess possible scaling and corrosion problems. By evaluation of the calculation of the saturation indexes severe scaling problems are not anticipated. They could happen quartz, anhydrite and calcite scales, their saturation indexes being positive, but not high values.

The hot water temperature into the reservoir has a bit higher value than the wellhead temperature. Through the surface can be a mixing of water from different feed zones, but in the deeper part of the well. If colder water from shallow feed zones mixes with hotter water from the deeper ones might be a higher supersaturation, but no high supersaturation was estimated.

A deposition sample formed during the last six years of well production was removed when a heat exchanger was mechanical cleaned and it was XRD analysed. It was found out quartz and carbonate crystals into the sample. These were estimated by simulation as well.

The corrosion behaviour of carbon steel in geothermal water from well 4796 was studied based on the polarization curves, on corrosion rate determination from gravimetric experiments and on the potential-time variation, at 80°C, in static and dynamic conditions.

From the polarization experiments results that the corrosion current density is equal with the dissolved oxygen diffusion limiting current density, the only cathodic thermodynamically possible reaction.

The carbon steel corrosion rate at 80°C decreases with the exposure time and attempts a steady value after 14 days, both in dynamic and static conditions. In dynamic conditions the corrosion rate is about 5 times higher than in static conditions.

The corrosion potentials shift to electropositive values with the exposure time, less in dynamic conditions, but the metal still remain in the active domain.

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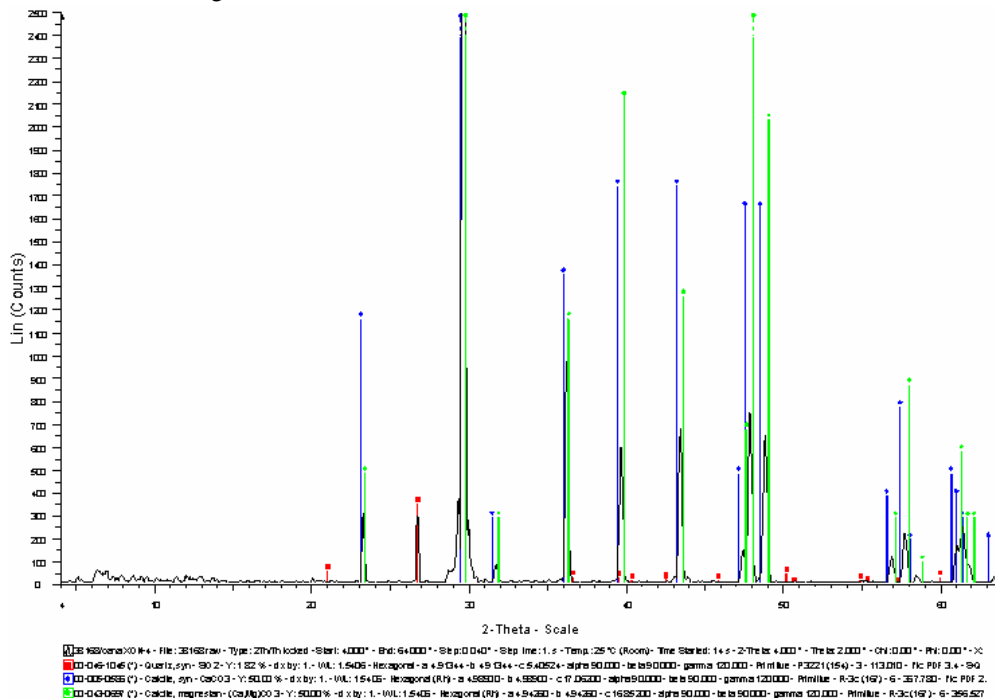
Figure 3. The XRD diagram for depositions from well4796.