

DIAGNOSIS METHODS USED TO ESTIMATE THE BEHAVIORAL MODE OF THE GEOTHERMAL FLUID, IN ALREADY RUNNING FACILITIES

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Abstract

The present paper wishes to be a succinct study dealing with the characterization possibilities of the behavior of geothermal waters, in the process of exploiting their thermal energy. There will be an analysis of the relations between the analytical data of the fluid and some theories from this field's literature, regarding the estimation of their characteristics. The validity of the latter will be verified through the actual determination of the corrosion rate of a certain type of steel, in the exploitation facility of the geothermal water extracted through well 4797 Oradea.

Key words: corrosion, deposits, estimation,

INTRODUCTION

The geothermal energy, as an unconventional type of energy, occupies a major role in the new development strategies of the World countries. The prognosis for the year 2020 by The World Energy Council shows that, in the case of a development direction based on ecological principles, the weight of the unconventional resources of energy will increase from 2 %, at present, to 13 %.

The reservoirs of thermal water are, in general, systems with continuous refilling, either naturally, or artificially, through re-injection. The geothermal energy is, therefore, to a great extent, renewable, and, at the same time, in a large measure, ecologically adequate.

An important aspect connected to exploiting the energy of geothermal waters is the identifying of specific problems that may arise: sediments coating or deposits, corrosion, presence of bacteria accentuating the two phenomena.

The specificity of the above is tied to aspects regarding the:

- physical and chemical characteristics of the geothermal fluid;
- highlighting the presence of some bacteria like those of the sulfate reductive type;
- conditions and mode of exploiting the reservoir;
- materials which compose the exploitation equipments.

MATERIALS AND METHODS

Physical and chemical characteristics of the geothermal fluid

The main factors which decide the action of the water on the transportation and usage installations (pipelines, storage tanks, heat exchangers) are: pH, quantity of bicarbonates, calcium ion concentration, free carbon dioxide content, oxygen, sulfurated hydrogen, temperature.

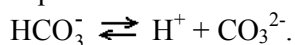
Along the years, there have been made a series of researches in order to establish coefficients which to allow the estimate, based on some analytical data of the waters, of either the embedded, or the aggressive character of the latter.

The first one to obtain credible results in this endeavor is Professor W.F. Langelier. On the basis of some analytical and easily accessible data of the water, he determines a mathematical expression linking those data and the water's pH balance.

$$\text{pH}_{\text{ech}} = (\text{pK} - \text{pK}_s) + \text{pCa} + \text{pAlc},$$

where:

K is the equilibrium constant for the equation:



Its expression is:
$$K = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}.$$

$$\text{pK} = -\lg K.$$

K_s is the equilibrium constant for the equation:



Its expression is: $K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}].$

$$\text{pK}_s = -\lg K_s.$$

$$\text{pCa} = -\lg[\text{Ca}^{2+}], \text{ where: } [\text{Ca}^{2+}] = \text{moles/l.}$$

From the values: of the pH balance and of the measured pH – is established the saturation coefficient, I_s, through the relation:

$$I_s = \text{pH}_{\text{meas}} - \text{pH}_{\text{ech}}.$$

Taking into account the value of the saturation coefficient, the waters can be classified as follows:

1. Waters with I_s > 0 are waters who tend to deposit CaCO₃;
2. Waters with I_s = 0 are waters in a state of balance – in what regards the carbonic species, but having the capability of corroding the installations;
3. Waters with I_s < 0 are waters with an aggressive character on CaCO₃, having the tendency to dissolve it.

The saturation coefficient calculated according to Langelier offers indications only about the quality degree of the water's development direction, without allowing any information about quantity. In order to

obtain some indications regarding quantity – in what concerns assessing the character of the water, was introduced, also, the stability coefficient, known as the Ryznard coefficient, having the following expression [1]:

$$I_{\text{stab}} = 2\text{pH}_{\text{ech}} - \text{pH}_{\text{meas}}$$

The stability coefficient shows the character of the water, that is:

1. $I_{\text{stab}} < 7$ – the water presents sediments;
2. $I_{\text{stab}} = 7$ – the water generates a slight protective coat;
3. $7 < I_{\text{stab}} < 9$ – the water is corrosive;
4. $I_{\text{stab}} > 9$ – the water is extremely corrosive.

Another relevant coefficient in this context is the one which characterizes the aggressiveness of the water towards the iron. According to calculations, sustained by the experimental results, the value of the pH until which the iron can be corroded is: 7.5 in cold waters and 8.3 in warm waters. Therefore, the difference between the 8.3 maximum pH value (the upper limit of the aggressiveness towards the iron) and the actual pH – gives us valuable information about the water's action on the iron. The bigger this mentioned difference, the more pronounced the corrosive character of the water will be. To obtain quantity regarding information, it is necessary to multiply the difference of the pH values with the concentration of the free carbon dioxide, expressed in mmols/l. [2, 3]

$$I = (\text{pH}_{\text{max}} - \text{pH}_{\text{actual}}) [\text{CO}_2 \text{ free}],$$

where:

$$\text{pH}_{\text{max}} = 8.3;$$

$\text{pH}_{\text{actual}}$ = the measured pH;

$[\text{CO}_2 \text{ free}]$ = the concentration of the free carbon dioxide - expressed in moles/l.

Considering the numerical values of this last coefficient, the waters can be classified as follows:

1. Geothermal waters with corrosive character:
 - a) very corrosive: $I \geq 10$;
 - b) corrosive: $1 \leq I < 10$;
 - c) slightly corrosive: $0.5 \leq I < 1$.
2. Geothermal waters with non-corrosive character and without the tendency to deposit CaCO_3 :
 - $-0.5 \leq I < 0.5$.
3. Geothermal waters with non-corrosive character, but with the tendency to deposit CaCO_3 :
 - a) with slight tendency to deposit: $-2 \leq I < 0.5$;
 - b) with moderate tendency to deposit: $-5 \leq I < -2$;
 - c) with increased tendency to deposit: $I < -5$.

It may happen that the stability coefficient regarding CaCO_3 shows a tendency to deposit, and the stability coefficient concerning iron indicates a tendency to corrosion. In this case, the water will corrode, in the beginning, the iron, with the corrosion rate diminishing as the CaCO_3 deposits.

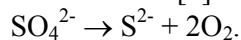
Another approach of the same problem was made by researchers Merrill and Sanks. They have established five quality conditions necessary in order for the water to form a protective layer of calcium carbonate. [4-6]

1. The water to be oversaturated with 4 to 10 milligrams of CaCO_3/l (0.04-0.1 mmol/l).
2. The concentrations of the calcium and bicarbonate ions to be upper the value of 0.8 mval/l and to have close values.
3. The molar concentrations of the species: bicarbonate, chloride and sulfate to meet the condition: $\text{HCO}_3^- / \text{Cl}^- + 2 \text{SO}_4^{2-} > 5$.
4. The pH of the water to be between 6.8 and 7.3.
5. The speed of the water in the pipelines to not exceed the value of 0.6 m/s.

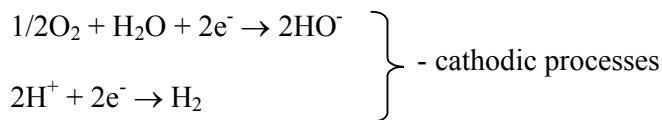
If these conditions are fulfilled, the layer of calcium carbonate formed is adherent and compact, thus ensuring the pipeline's protection against corrosion. The two researchers recommend, first of all, fulfilling the first three conditions.

Highlighting the presence of some bacteria like those of the sulfate reductive type

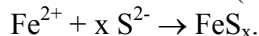
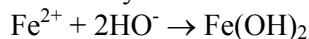
In the case of the geothermal waters containing sulfate ions, in the absence of oxygen – in the corrosive action can take part the presence of some bacteria of the sulfate reductive type, capable of reducing the sulfate ion to the sulfide ion [7]:



The obtained oxygen can play the role of a cathodic depolarizer. The presence of the sulfide ion accelerates the corrosion by moving the potential of the steel towards more negative values, thus making possible the corrosion through a depolarization of mixture.



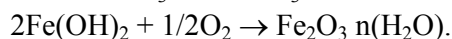
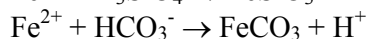
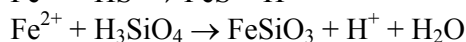
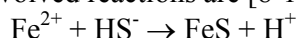
Secondary reactions:



There are studies which incriminate the biological factor in the increase of the corrosion rate, especially of the pointed one and of the stress corrosion.

The formed sulfides can have various chemical formulas, of stoichiometric nature or not, and can present themselves in different forms of crystallization or can be amorphous.

The simultaneous presence of the Fe^{2+} ion and of the chemical species: H_2S , CO_3^{2-} and SiO_2 – can lead to the direct or indirect forming of some insoluble compounds that are depositing on the surface of the metal. The involved reactions are [8-10]:



The materials which compose the exploitation equipments

Generally, the geothermal waters contain a series of gases or substances – in dissolved form, the behavior of which – during the exploitation cycle – can cause the destruction of the metallic surfaces through corrosion.

The chemical species usually present in these waters, and which can cause corrosion (especially of the carbon steel) are: oxygen (it appears in the exploitation installations of geothermal waters, through ventilation processes, as a result of certain manipulation procedures that cannot be avoided: shutdown-starting up, valve sealing, etc.), hydrogen ions, chlorides, sulfides, carbon dioxide, ammonium ion, sulfate ion (which, all, intervene in both the corrosion inside the well and the corrosion of the transportation and usage installations).

The experiments shown in this paper have the goal to estimate the embedding or aggressive character of the water delivered by well 4797 Oradea and to compare the results of the estimate with those of some practical surveys.

For this purpose, we have made a physical and chemical analysis of the thermal fluid at drill exit, after degasification. On the basis of the analytical data, we have calculated the pH balance and the saturation and stability coefficients. Their value has allowed us to theoretically estimate the character of the water. In order to study the phenomena which occur, in reality, in the systems of transportation and usage of the water, we have done an “in situ” measuring of the steel OLT 45R, material frequently used in such facilities. The corrosion rate has been quantized through the gravimetric and penetration indexes.

RESULTS AND DISCUSSIONS

In the physical and chemical analysis of the geothermal water have been identified the main anions and cations which intervene in the estimate calculations of the water's character, and have been specified on place and analyzed in laboratory – the main dissolved gases, involved in the transformations suffered by the water in the exploitation circuit.

The results of the analyses are presented in table nr. 1.

Table 1

The values of the main indexes, identified during the experiment

Main indexes/coefficients	Measuring Unit	Value
pH	l unit	7.2
Bicarbonates	mg/l	153.80
Chlorides	mg/l	10.30
Sulfates	mg/l	664.60
Calcium	mg/l	296.60
Magnesium	mg/l	21.90
Total sulfides	mg/l	2.31
Sulfurated hydrogen	mg/l	0.55
Dissolved oxygen	mg/l	3.39
Free carbon dioxide	mg/l	7.29

The calculated pH balance has the value 6.75. Taking into account this value and the identified actual pH, we can determine the following two coefficients: $I_{\text{sat.}} = 0.45$ $I_{\text{stab.}} = 6.3$

For a positive saturation coefficient, the water has an embedding character, and for a stability coefficient between 6 and 7, the water deposits a slight protective layer. To study the phenomena which occur, in reality, in the systems of transportation of the thermal water, we have inserted the experimental device on a pipe section that conducts the thermal water from degasifiers, through pumping, to the entrance in the heat exchangers.

The results of the trials are shown in tables 2 and 3.

Table 2

The masses of the samples used in the experiment (g)

Exposure	Initial mass	Mass with deposits	Mass without deposits
30 days	14.3427	14.2081	14.1732
60 days	14.5749	14.5142	14.0693
90 days	14.4342	13.9445	13.2083

Table 3

The corrosion rates for the steel OLT 45R

Time interval (days)	Corrosion rates (g/m ² /day)	Corrosion rates (mm/year)
30	8.235	0.417
60	11.584	0.587
90	19.270	0.997

The corrosion rate of the steel OLT 45R increases continuously, from 0.417 mm/year at the first pipe section, until 0.977 mm/year, after 90 days, approaching the passage limit towards the resistance class which includes steels of little stability. The layer of compounds deposited on the surface of the sample, having a brown-reddish color, is in a continuous growth during the experiment, yet without ensuring the necessary protection against corrosion, probably because of its porosity.

The theoretical evaluation of the water's character, made at the beginning of the experiment, has highlighted the slightly embedding character of this water, which allows the forming of a protective layer of calcium carbonate on the metal surfaces exposed to the thermal environment. Yet, the corrosion products do not have a good adhesion to the metallic surface, and, instead of offering it protection, on the contrary, they enhance the deployment intensity of the oxidation and reduction processes.

In concordance with the results of the practical experiments, we can rather assert that the water has a moderately aggressive (corrosive) character, and that although there is a relatively consistent layer of deposits, it does not provide protection against corrosion.

Estimating the behavior of geothermal waters in the exploitation installations, on the basis of the physical and chemical characteristics of the fluid, is not always illustrative. The particularities of the exploitation mode have, also, a decisive say.

The corrosion rate in the case of the steel OLT 45R exceeds, after 90 days of immersion, the value of 0.9 mm/year, over which, according to the corrosion resistance's decimal degrees scale, the steels are rated little stable. It is probable that this value be even surpassed as the immersion time increases, because during the experiment the corrosion rate has risen continuously.

CONCLUSIONS

We can conclude that, in the given situation, the most aggressive species in initiating the corrosion is the oxygen, which, in the geothermal environment, reduces itself to O^{2-} , simultaneously with the iron's ionization

to ferrous ion. The latter is found in a concentration of 3.39 mg/l at the well in Oradea. After the initiation of the process, an important role in the rate with which the corrosion develops is played by the nature of the products deposited on the metal surfaces. As the experimental data show, the layer of products deposited on the samples which have been immersed in the water of well 4797 Oradea – does not ensure the protection of the metal wall. The products, though in large quantity, are porous enough as to still allow, on the coated areas - the expansion of the iron oxidation reaction, and, on those areas where there is a relatively good access of the water - the development of the reduction reactions. The existent potential difference between the free and the coated areas is a real engine servicing the unrolling of corrosion. The fact that the products have a porous consistency favors their detachment from the metal walls as a result of the fluid's flow.

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