

AN ESTIMATION OF CORROSION BEHAVIOUR FOR GEOHERMAL WATER TRANSPORT AND STORAGE EQUIPMENT IN BIHOR COUNTY, ROMANIA

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Abstract

Geothermal water is a two-phase fluid having a liquid phase and a gas phase, and this is the reason that any attempt for use has to solve practical obligatory one of the following problems, both maybe: scale sedimentation and/or corrosive action. Geothermal waters of Bihor county contain in liquid phase: bicarbonates, sulphates, chlorides, calcium, magnesium, sodium, potassium and iron ions, phenols. Dissolved gases are: carbone dioxide, methane and hydrogen sulphide.

This paper has a purpose the estimation of geothermal water's character according to the specific physical and chemical parameters. For this purpose I have chosen a few representative wells out of the geothermal collectors in Bihor county. The physical and chemical analysis necessary for calculating the equilibrium parameters have been done. The temperature and the pH have been measured and CO_2 , HCO_3^- , CO_3^{2-} , H_2S , S^{2-} have been dosed. I have calculated the CO_2 equilibrium, pH equilibrium values, saturation index and stability index for these specific wells. As a result of these calculations I have drawn orientative conclusions about the corrosion behaviour of the metalical materials used for geothermal water transport and storage equipment

Key words: scale sedimentation, corrosion estimation, equilibrium parameters.

INTRODUCTION

The most accesible way to use the internal energy of the Earth is the geothermal water. These are the main transmission agent of geothermal energy to the surface.

Thermal waters are waters of which self temperature is independent on the emerging place, 4 °C higher than the mean air temperature and 2 °C higher than the mean earth temperature.

In Bihor county there are two important geothermal water systems: the Superior Pannonian deposit - the most important as proportions and reserves - and the mesosoical limestone and dolomyth deposit in the: Băile Felix, Băile 1 Mai, Oradea, Borș area.

The physical, chemical and thermodynamical properties of the geothermal waters cause many problems to the exploitation. Geothermal water is a two-phase fluid having a liquid phase and a gas phase, and this is the reason why any attempt to usage has to solve almost obligatory one of the following problems, both maybe: scale sedimentation and/or corrosive action.

MATERIAL AND METHODS

A primary index used to estimate the water character is the concentration of free CO₂. Comparing this with the concentration of equilibrium CO₂ calculated by the Tillman-Heublein (Tillmans, 1932) formula:

$$[\text{CO}_2]_{\text{eq.}} = \frac{[\text{CO}_{2,\text{bound}}]^3}{K_t}$$

$$K_t = 66270 \cdot (0.9714)^t \quad t = \text{temperature in } ^\circ\text{C}$$

we get information about water characters.

The establishing of free CO₂ content, especially for geothermal waters, is often affected by errors. So there were sought other indexes to characterize the equilibrium state (Frank E. Clarke, 1980).

W.F. Langelier establishes an equation to calculate the equilibrium pH using some more accessible analytical data. For a given water composition the equilibrium pH is defined as the pH value which water doesn't dissolve and doesn't fall out carbonate. (Langelier W.F., 1946)

The equilibrium, that establish in the CaCO₃-CO₂-H₂O-system, is

$$K[\text{CO}_2] = [\text{H}^+] \cdot f_m \cdot [\text{HCO}_3^-] \cdot f_m$$

$$K[\text{HCO}_3^-] \cdot f_m = [\text{H}^+] \cdot f_m \cdot [\text{CO}_3^{2-}] \cdot f_d$$

$$K_s = [\text{Ca}^{2+}] \cdot f_d \cdot [\text{CO}_3^{2-}] \cdot f_d$$

f_m, f_d - activity factors of monovalent respectively bivalent ions.

These equations give the equation for the equilibrium pH:

$$\text{pH}_{\text{eq.}} = \text{pK} - \text{pK}_s + \text{pCa}^{2+} + \text{pAlk} - \lg f_d$$

The concentration of Ca²⁺ ions is given in mol/l, the alkalinity in equivalent/l titratable base in the presence of methylorange.

$$-\lg f_d = 0.5 \cdot z_i^2 \cdot \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2 \cdot \mu \right)$$

$$z_i = 2$$

$$\mu = 0.5 \cdot \sum_{i=1}^n c_i \cdot z_i^2$$

c_i - the concentration of species i in mol/l

z_i - the valence of species i

$$\text{pK} = 2902.39 / T + 0.02379 \cdot T - 6.494$$

T - temperature in $^\circ\text{K}$

$$\text{pK}_s = 0.01183 \cdot t + 8.03$$

t - temperature in $^\circ\text{C}$

Comparing the two values (measured pH and equilibrium pH) an important index results, the saturation index (I_{sat}):

$$I_{\text{sat}} = \text{pH}_{\text{meas.}} - \text{pH}_{\text{eq.}}$$

By the value of the saturation index waters can be classified the following way:

- 1.) $I_{\text{sat}} > 0$ - waters with inlaying character;
- 2.) $I_{\text{sat}} = 0$ - balanced waters from the viewpoint of carbonical species;
- 3.) $I_{\text{sat}} < 0$ - waters with aggressive character to CaCO_3 and metallic materials.

Considering that the saturation index gives qualitative information only, was proposed a new empirical calculation expression (Ryznar, 1994) for another index, the stability index ($I_{\text{stab.}}$):

$$I_{\text{stab.}} = 2 \cdot \text{pH}_{\text{eq.}} - \text{pH}_{\text{meas.}}$$

In accordance to this a water with:

- $I_{\text{stab.}} \leq 6$ - presents crusts;
- $I_{\text{stab.}} = 7$ - generates a lightly protective layer;
- $I_{\text{stab.}} > 7$ - is corrosive;
- $I_{\text{stab.}} \geq 9$ - is very corrosive.

In an article published in 1977 the researchers D.A. Merrill and R.L. Sanks formulated 5 conditions concerning the water composition and the possibility of forming protective CaCO_3 layers.

Out of the 5 conditions, the first three of them are the most important for obtaining adherent and compact layers.

1. the water must be oversaturated then CaCO_3 , with 0.04-0.1 mmol/l;
2. the concentrations of the calcium and bicarbonate ions must be higher than 0.8 mmol/l;
3. there must be the following equation between the molar concentrations of bicarbonate, sulphate and chloride ions [HCO_3^-];
4. the water pH must have the values 6.8-7.3;
5. the water speed of flowing through the pipes (installation) must be higher than 0,6 m/s.

RESULTS AND DISCUSSION

The present work intends comparing information got by estimating the water character based on the saturation and stability indexes with the data collected from the site and by laboratory measurements.

There were chosen all the wells from three thermal water collectors: Tryas, Kreta, Pannonian. It must be mentioned that waters from different sources have different physical and chemical characters. The shortly characterisation of the three types of waters is the following:

- a.) The waters in Triassic collectors (Oradea zone)
- have a temperature of 74-101 °C;
 - general chemical character: sulphato-carbonato-chalco-magnesian;
 - mineralisation: ≈ 1 g/l.
- b.) The waters in Cretacic collectors (Băile Felix, Băile 1 Mai zone)
- have a temperature of 33-49 °C;
 - general chemical character: bicarbonato-sulphato-chalco-magnesian;
 - mineralisation: ≈ 0.7 g/l.

Table 1

Physical and chemical characters of the studies wells

Well → ↓mg/l	4004 Oradea	4005 Oradea	4006 Oradea	4155 Borş	4058 Săcuieni	752 Săcuieni	4003 Felix	Ciu me- ghiu
Cl ⁻	17,3	17,63	19,50	5632,07	836,84	744,66	14,22	528, 95
HCO ₃ ⁻	203,06	168,45	166,37	1573,80	2951,91	2951,91	548,8 1	3355 ,0
SO ₄ ²⁻	546,88	702,02	674,03	12599	sld	13,16	102,0 0	45,2 6
Na ⁺	30,00	21,00	35,0	4252,53	1650,00	1550,00	49,41	1587 ,28
Ca ²⁺	178,56	244,00	223,45	41,45	14,43	7,1	141,0 2	23,5 8
Mg ²⁺	62,32	30,71	43,65	3,28	4,26	4,80	28,15 4	2,62
pH	6,6	7,1	6,9	6,8	7,2	7,3	7,5	8,3
t [°C]	80	90	81	106	78	64	44	100
Ionic streng th × 10 ⁻³	53,00	60,59	60,12	194,22	73,97	70,48	28,00	74,0 0

- c.) The waters in Pannonian collectors:
- have a temperature of 25-80 °C;
 - general chemical character: hardly carbonated or hardly chlorinated, but having Na⁺ as major cation;
 - mineralisation: 3-10 mg/l;
 - accompanied by considerable quantities of gases: CH₄, CO₂, H₂S.

In this work we have monitored following 8 wells: well No. 4005, 4006 Oradea; well No. 4155 Borş; well No. 4003 Felix, Ciumeghiu; well No. 4058 and No. 752 Săcuieni.

For all these wells there were calculated: ion strength, pK, pK_s, -lg f_d values, equilibrium pH and the two indexes: saturation index and stability index, in conformity with equations. Data about water composition and

calculated data are shown in tables 1 and 2. The aggressive or inlaying character of the waters has been studied during the years, trying to determinate mathematical relations which can estimate the waters behaviour when in contact with metallic materials. Because of the fact that in the natural waters the calcium and bicarbonate ions are usually involved in forming protective layers, the estimated mathematical relations have been determined from the equilibrium between the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ species.

Table 2

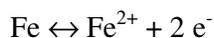
Aproximated values for I_{sat} , and I_{stab} , calculated for the two wells at the entrance and emergence of water in/from installation

Well → Calculated or measured value ↓	4004 Oradea	4005 Oradea	4006 Oradea	4155 Borş	4058 Săcuieni	752 Săcuie ni	4003 Felix	Ciume- ghiu
pH_{max}	6.6	7.1	6.9	6.8	7.2	7.3	7.5	8.3
pH_{eq} , by t °C entrance (warm)	5.72	7.49	6.03	6.22	6.26	6.46	5.85	5.53
I_{sat} , by t °C entrance (warm)	+ 0.88	- 0.39	+ 0.87	+ 0.58	+ 0.94	0.84	1.65	2.77
I_{stab} , by t °C entrance (warm)	4.84	7.88	5.16	5.64	5.32	5.62	4.20	2.76
pH_{eq} , by t °C exit * (cold)	6.64	8.19	6.61	7.05	6.80	6.84	6.32	6.31
I_{sat} , by t °C exit (cold)	- 0.04	- 1.09	+ 0.29	- 0.25	+ 0.40	+ 0.46	+ 1.18*	+ 1.99
I_{stab} , by t °C exit (cold)	6.68	9.28	6.32	7.30	6.40	6.38	5.14	4.32
Penetration index [mm/year]	0.312	0.802	0.249	0.680	0.990	0.770	0.530	0.383

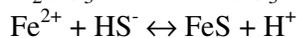
By the few selected and presented data the water character for the 8 wells can be defined in accordance to the criteria accepted by the literature.

Geothermal waters of Bihor county contain in liquid phase: bicarbonates, sulphates, chlorides, calcium, magnesium, sodium, potassium and iron ions, silicone dioxide, phenols. Dissolved gases are: carbone dioxide, methane and hydrogen sulphide.

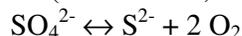
Considering the presence of CO_2 , H_2S , pH 6.8-8.3 and oxygen deficiency, we can imagine an iron corrosion mechanism with hydrogen depolarisation, shown in the equations below:



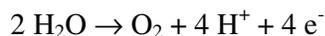
and the secondary reactions:



In the case of geothermal waters with sulphates content in the absence of oxygen the existence of some sulphate-reducer bacteria may be involved in the corrosive action, these bacteria are able to reduce the sulphate ion to sulphide (YuPo J. Lin, et al.2001):



The oxygen is here the cathode depolariser, in accordance to the reaction:



The presence of S^{2-} ion accelerates the corrosion by changing the steel potential to more negative values. The corrosion takes place by a mixed depolarisation of hydrogen and oxygen.

The formation of carbonate scales is possible due to this reaction:



Having in view all these reactions and the fact that some of them can become prevalent at some point, we can deduce that water can have either an inlaying or a corrosive character to the metal materials of transport or using installation.

From the calculated data it can be observed that, at the temperature of these waters when entering the installation, the saturation indexes and stability indexes show one water only as having a corrosive character: water of well No. 4005 Oradea. For the rest of the wells the indexes show an inlaying character: increased at the Ciumeghiu and well No. 4004 Oradea and temperate for the others.

The estimative calculations made for waters when emerging the heating installation (20 °C for well No. 4003 Felix and 40 °C for the rest of the wells) show an increasing aggressive character of these waters relative to cool-down. In this situation there are two waters with a stability index greater than 7: well No. 4005 Oradea ($I_{\text{stab.}} > 9$ - very corrosive waters) and well No. 4155 Borş ($I_{\text{stab.}} > 7$ - corrosive water).

The penetration indexes determined by laboratory conditions are in relative accordance to the estimated indexes. These values are great enough for the two wells with corrosive waters, but less than penetration indexes of Săcuieni wells. Penetration indexes decrease in this order: 4058 Săcuieni,

4005 Oradea, 752 Săcuieni, 4155 Borș, 4003 Felix, Ciumeghiu, 4004 Oradea, 4006 Oradea.

The saturation and stability indexes take into account the water pH and the content in carbonic species only. In the case of geothermal waters we must have in view other aspects, too, in order to get a better correlation between the composition and the aggressive character of the waters. These aspects are: high mineralisation, high Cl^- content, (in Borș, Săcuieni, Ciumeghiu areas) and the appearance of hydrogen sulphide, especially in Săcuieni area. These characters increase the aggressive character of water, but they are ignored in the used formulas.

High mineralisation and temperatures cause an increase of corrosion speed. Both factors have the same action: high mineralisation causes an increase of conductivity; high temperature increases the speed of the two electrochemical corrosion processes and makes that protective CaCO_3 layer loses its protective character in some places (Merrill, D.T., Sanks, R.L., 1977 Reed B. W. et al. 2008,).

The presence of Cl^- ion makes the water corrosive for usual alloys of iron (Leon Gosar, Darko Drev, 2011). About Cl^- and Na^+ ions, waters in Borș have a sea water alike composition (48.43 % Cl^- and 36.6 % Na^+). The characteristic type of corrosion that appears after destroying the protective layers by the Cl^- is *pitting*. This is the most often corrosion type met in the case of the installation in Borș area.

Other complications to estimating aggressivity result from the presence of H_2S and possible presence of sulphate-reducer bacteria (*sporovibrio desulfuricans*) (Ismail Andijani, Anees u. Malik, 2004). These grow well in anaerob conditions, at pH 5.5-8.5 and relatively high temperatures (60-80 °C) (Rădoi, 1982, J. Starosvetsky, 2007). They reduce sulphates in the presence of hydrogen and organical substances. This is a possible explanation for the sufficient intensive corrosion in Săcuieni zone that seems to become more intensive in these times. The water deposit in this zone is near a hydrocarbone layer. Increasing corrosion could be explained by a polyphosphate type inlaying inhibitor used to hold in equilibrium the $\text{CaCO}_3\text{-C}(\text{HCO}_3)_2$ system (Ohl, P.C. et al. 2001). It seems that this inhibitor dissolves the old carbonate crust and offers to water the possibility to contact the metall.

CONCLUSIONS

Finally we can stress the following aspects:

- applying the usual methods to characterise waters according to their aggressivity, only relative real data can be obtained;
- a more exact characterisation must be made in a larger context having in view many characteristic local elements, like the

- presence of bacteria or of hydrocarbone deposits near the geothermal water layer;
- in the quantitative estimations not all the factors that contribute to the aggressivity of water can be taken into account.

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