

SYNTHESIS REGARDING THE PROBLEM OF DEPOSITS AT THE GEOTHERMAL WELLS IN BIHOR DISTRICT-ROMANIA

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ABSTRACT

The methods of scaling elimination or control it, differ from field to field, from site to site and the range from adding scale inhibitors to the geothermal fluid to maintaining the equilibrium is according to the specific condition of the site.

The paper objective is to share the results obtained in some laboratory tests and some experimental field tests to prevent scaling.

The zones of this investigation are parts of Bihor district. The surface of district is 7535 km² and it is situated in the northwest of Romania.

INTRODUCTION

The research done so far regarding the chemical compositions of the geothermal waters in Bihor district have revealed that on this area there are three types of geothermal water according to the geological reservoir. In the area Felix -1Mai, the geothermal waters are belonging to the Cretaceous reservoir, of a bicarbonate-sulphate-calcium-magnesium type; in Oradea area there are geothermal waters belong to the Triassic reservoir, of sulphate-bicarbonate- calcium-magnesium type. The geothermal waters from the two above-mentioned reservoirs are not strongly mineralised, having the (Total dissolved salt) TDS= 0.4 –1.0 ppm. As an exception, should mention the geothermal waters from Bors area, which are in a Triassic reservoir but are chloride sodium type, TDS = 10-15 ppm. In the north and the south of the Bihor district there are geothermal waters belonging of Pannonian reservoir, waters of different types (in majority bicarbonate -chlorine-sodium type, and some of chloride sodium type). The TDS = 3 –15 ppm. The well from Sarcau should be mentioned as

an exception. This has an extreme mineralisation, the TDS = 30 ppm.

If the geothermal waters form Triassic and Cretaceous reservoirs do not set problems with respect to the scaling, the waters from Pannonian shall raise this delicate problem. A strengthens exception must be note. As well, [for the Triassic reservoir]: the geothermal waters from Bors perimeter that have –the way we have already presented –unusual chemical composition compared to those from Oradea. The geothermal waters belonging to Bors generate massive deposits.

In the Pannonian reservoir, the areas where the wells have scaling are the following: areas north from Oradea, Marghita, Sacuieni perimeter; and south from Oradea: Salonta area.

Table 1. Presents the major physique-chemical characteristics of the geothermal waters.

The research done have shown that these geothermal waters are unstable from the chemical point of view, manifesting the tendency of depositing scales, crusts during changing initial conditions of pressure and temperature. There was notice even the tendency of aggressiveness (corrosion) towards the ferrous metals with which they come into contact (equipment).

In certain cases the deposits (on Bors area the deposits are so massive, that they lead to block the exploitation equipment, implying thus stopping the wells from production.

Theoretical aspects regarding the deposits and corrosion phenomenon

The crust deposits, as the corrosion are two closely linked phenomena and there are the determined by the character of geothermal water and its temperature.

The moment when the geothermal water leaves the aquifers the physical-chemical equilibrium of the fluid is altered. As a result the crust deposits appear

on the transport pipes, especially after getting out of the well.

The phenomenon of corrosion of the metallic surfaces at the exploitation equipment can also be seen.

According to the composition of geothermal fluid the most frequent substance which forms crusts is the calcium carbonate. This is not to be found in water, but it is formed from out of bicarbonate ions (HCO_3^-) and calcium ions (Ca^{2+}) from the geothermal water as a result of altering the mentioned equilibrium.

This shifts the equilibrium between bicarbonate and carbonate.

The presence of the bicarbonate ion claims the presence of a well-definite quantity of carbon dioxide

dissolved in the water. The concentration of carbon dioxide over certain limits determines the corrosive action of respective water.

In the gaseous carbonated systems take place the following reactions:

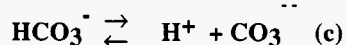
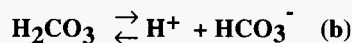
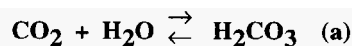


Table 1. The physique-chemical characteristics of geothermal water sources of the area

Source Characteristics	Oradea	Felix	Bors	Pannonian aquifer		
				Sacuieni	Marghita	Salonta
Temp (°C)	70 – 102	40 – 89	115 – 120	74 – 85	75 – 80	75 – 80
pH	6.2 – 7.3	6.5 – 7.5	7.0 – 7.8	7.6 – 7.8	7.0 – 7.8	7.3 – 7.9
TDS (ppm)	0.85 – 1.4	450 – 750	9.5 – 14.1	5.5 – 7.3	2.3 – 2.6	4.6 – 5.07
SiO ₂ (ppm)	45 – 74	30 – 55	60 – 168	50 – 65	40 – 45	50 – 68
HBO ₂ (ppm)	abs.	abs.	175 – 305	50 – 190	15 – 27	90 – 110
Hardness (°germ.)	35 – 48	16 – 30	15 – 25	1.2 – 2.3	1.5 – 2.9	2.5 – 3.0
Phenol (ppm)	abs.	abs.	0.3 – 0.7	4.6 – 8	0.3 – 0.7	9.5 – 10
Cl (ppm)	15 – 50	10 – 27	6000 – 7100	420 – 850	500 – 2300	640 – 700
SO ₄ (ppm)	360 – 850	90 – 240	125 – 170	14 – 27	700 – 820	45 – 50
HCO ₃ ⁻ (ppm)	150 – 300	360 – 420	1200 – 1700	2300 – 2900	1300 – 475	2900 – 3300
Na ⁺ (ppm)	30 – 75	15 – 25	3800 – 4900	1300 – 1500	900 – 1050	1100 – 1600
K ⁺ (ppm)	3 – 15	2 – 8	300 – 470	20 – 40	8 – 18	20 – 50
NH ₄ ⁺⁺ (ppm)	0.8 – 2.2	0.5 – 0.9	10 – 16	0.6 – 3	6 – 9	8 – 20
Ca ⁺⁺ (ppm)	144 – 250	55 – 200	84 – 181	6 – 12	3.5 – 7.58	12 – 18
Mg ⁺⁺ (ppm)	25 – 62	14 – 25	12 – 70	0.6 – 4	2 – 5	2.9 – 4
Fe ⁺⁺ (ppm)	0.7 – 3.4	0.07 – 3.4	1.7 – 3.0	0.18 – 2	0.25 – 4	0.2 – 0.8
Water Type	Ca SO ₄	Ca (CO ₃) ₂	NaCl	NaHCO ₃	NaHCO ₃	NaHCO ₃

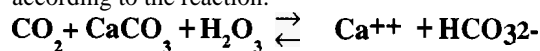
The equilibrium constant that reflects the sum of these reactions is:

$$K_a = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]}$$

$$K_b = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$K_c = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

In the case of the closed systems the concentration of dissolved carbon dioxide is dependent on the concentration of the ions of calcium in the solution. The quantity of carbon dioxide dissolved necessary for maintaining the ions of calcium in solution is according to the reaction:



The last term is so called afferent carbon trioxide.

At a given content of bicarbonates, the afferent carbon trioxide is dependent on temperature (it goes

up once with rising of temperature). At the same time, carbon dioxide is dependent on the contents of bicarbonates. In conclusion, the geothermal waters with a certain value of temperature and high bicarbonate contents reclaim high value of afferent carbon dioxide.

In the open systems (water in contact with the atmosphere) the solubility of CO₂ is low (the partial pressure of CO₂ is low too).

The water loses the carbon dioxide and the equilibrium of the above-mentioned reaction is altered, the higher contact with the atmosphere conduct to the greater quantity of lost CO₂.

Therefore, in the case which a water contents CO₂ in excess at low temperature, with the temperature going up, it can appear a carbon dioxide deficit. The bicarbonates decompose and calcium bicarbonate is formed.

Water that at high temperature does not contain CO₂ in excess (aggressive CO₂), by the falling of temperature the afferent carbon dioxide decreases and the water shall thus contain CO₂ in excess, becoming aggressive.

The corrosion being closely connected from a chemical point of view to the forming of crusts, the factors that determine its appearance are:

The temperature variation, aggressive CO₂ contents in water, high contents of mineral salts (chlorides) the flow speed within the installations, the existence of elbow, the oxygen dissolved in water.

Conclusively, in order to avoid the unwanted phenomena, the suggested solution, which solves avoiding altering the equilibrium of the geothermal fluid, is that of the exploitation in doublet.

Another solution would be that of using the inhibitors, where the systems of doublets cannot be applied.

Practical aspects regarding the removal of the deposits at the wells from Bihor District

The way we have presented at the beginning the deposit phenomenon with the geothermal wells in Bihor appears in Marghita, Sacuieni and Salonta this phenomenon is striking.

The chemical analysis of the crust drawn from the well in the area Bors has yield the following result: Ca₂CO₃ 91 - 95 %; Mg₂CO₃ 0,58 -3,04 %; Fe₂O₃ 0,95 -2,06 %; SiO₂ 0,16 -2,06 %; CaSO₄ 0,41-1,61%.

In order to prevent these phenomena right from the first chemical analyses of water at the first chemical analyses of water at the newly dug wells, there must be established whether the respective waters have a corrosive or scaling character, or its is passive from

this point of view. In this respect the quality of the geothermal water should be determined the CO₂ concentration (afferent and aggressive) and then according to these data, the proper inhibitors (should) be chosen, for the settled well.

The antecedent parameters must be also controlled during the exploitation, because there were cases when the deposits were not observed from the beginning, but they appeared afterward.

Out of the various means and methods in the specialty literature- of removing this phenomenon, we have chosen the treatment of geothermal waters with inhibitors.

In the case of the geothermal wells in Bihor district a treatment had been tried with inhibitors in watery solutions of low concentrations, which are continuously injected in the well, at a certain depth established by calculation. -The depth where the afferent CO₂ still maintains itself in the solution of the geothermal water.

The solution of inhibitor is injected at different depth using a dosing pump.

The concentration of inhibitors solutions have been established by laboratory tests from 2 mg/L, up to maximum 20 mg/L and were confirmed by tests that have been done on the field.

It was used the different inhibitors as: sodium-tripolyphosphate (TPNa); the ammonium salt of the copolymer of the maleic anhydride -commercial name VAMA, and an other product commercial name PONILIT. The last it is an organic chemical product, in fact a crystal modifier.

The control of scaling was performed by means of tests tubes fixed on a bypass at one outlet of the well.

Out of the acquired experience one can conclude that the TPNa is efficient in the case of the wells having temperatures bellow 90°C and a moderate mineralisation. This has yielded very good result in Marghita, S•cuieni and Salonta geothermal fields, in doses of 5 mg/L.

For the highly mineralized waters and with high temperatures (120°C), there is the case of Bors geothermal field; the best results had the treatment with the organic-type inhibitors. The both inhibitors have proved to be the efficient (VAMA and PONILIT). The test treatments with inhibitors have been made here quite a long time, over 2 years, and the established doses for the inhibitor solutions were of 10mg/L for VAMA and 2 mg/L for PONILIT.

As an observation the last one inhibitor has proved to be more efficient than VAMA (as can be seen the concentration in solution is lower, but the other extreme has reached the product proving to be

corrosive for the non-alloyed steels, out of which the well's equipment are made.

Conclusions

The treatments with inhibitors experienced to the wells have yielded results. I.e. the scaling have been considerably reduced, but they haven't been removed for good, that is the reason why we consider as being necessary carrying on the study with other inhibitors, as well, and also trying other methods of preventing the scaling.

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