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Corrosion Tests and the Use of Inhibitors in Low Temperature Geothermal Waters

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ABSTRACT

This paper emphasizes low temperature geothermal wells from Romania and Iceland. The main aim when operating a production well is to have continuous operation. Corrosion and scaling on the equipments surfaces is one of the biggest problems during geothermal water utilization.

Results of corrosion tests conducted on a selection of four metallic coupons that have been placed in the water circuit at Felix, Romania are described. Corrosion tests were conducted using aluminium, carbon steel, stainless steel, cast iron coupons involving different exposure periods to fluids. Scale deposition caused by corrosion and mineral precipitation from the water was chemical and XRD analysed.

A geothermal production well from Sudureyri, Iceland, which encountered almost similar type of deposits, was taken for testing of chemical inhibitors to combat scale. The test method developed for and used in this study provides a mechanism of deposit control by additives.

1. INTRODUCTION

Felix geothermal resort located at about 6 km to Oradea is the most useful place for balneological treatment in Romania. The water springing up at Felix comes from the lower cretaceous system. Felix Spa has a large experience in treating degenerative and inflammatory rheumatism – an experience based on a cure methodology specific to this resort. As a result of the medical research and experiments the following diseases are treated at Felix: chronical inflammatory rheumatism, rheumatismal degenerative diseases, post-traumatic diseases, troubles of the nervous system, associated diseases of the main profiles mentioned above.

Sudureyri is a small town located north-western of Iceland. The main users of the geothermal resources are swimming pool, fish drying, houses, kindergartens, church, shop, primary school. The well taken for study has been exploited at a capacity of 2.4 MW. The well depth is 684 m and the flowrate is about 10 l/s. The wellhead temperature is 67^0C.

2. SCALE AND CORROSION-LITERATURE REVIEW

Depending on the chemical composition of the geothermal well fluids, different types of scales are found in various geothermal areas. Damage in the exploitation equipments can occur in the form of metal corrosion and deposition on material surfaces of scale species. Once the geothermal water is available for use, prevention of scaling and corrosion is very important. Calcite, silica and sulphide are the most common solid depositions encountered in geothermal systems (Ungemach, 2001). Corrosive products are a second source of scale forming species.

The species of interest related to corrosion are hydrogen ion, chloride, hydrogen sulphide, carbon dioxide, oxygen. The corrosion rates of most materials increase as pH decrease. A pH below 6.5 in water with high CO_2 content makes possible a stress corrosion cracking of iron and steel. Higher values than 8 are usually associated with water that causes localized pitting, especially if dissolved oxygen is present. It may be possible to be associated with carbonate deposits. A very low concentration of 5 to 10 ppm Cl^- in the presence of oxygen can promote stress corrosion cracking in stainless steel. A high chloride concentration increases the solubility of iron in geothermal water by forming highly soluble complexes with the ferric ion.

A low concentration of hydrogen sulphide may have corrosion effect especially on Cu and Ni alloys. The threshold concentration for attack is less than 30 ppb H_2S. The presence of hydrogen sulphide in low temperature geothermal water could be a reason to suspect the existence of sulphide-reducing bacteria.

Carbon dioxide occurs naturally in many geothermal waters and has a major corrosive effect on steel. It has been noticed a very high uniform corrosion rate in the presence of carbon dioxide and sodium chloride up to 80^0C. An elevated temperature is most damaging to well water of high carbon dioxide content and low pH.

Oxygen is present in low concentrations in geothermal waters, but even traces of this gas accelerate corrosion (Opondo, 2002). The geothermal water may come into contact with the atmosphere during re-injection or if pumps other than downhole submersibles or oxygen might be one of the natural components in a gas accompanying the water. The corrosion of carbon steels is sensitive to very low concentration of oxygen. Together with chloride ion, oxygen can initiate stress corrosion cracking. A concentration that exceeds 15 ppb of oxygen in hot water is needed to cause localized corrosion and pitting. At low oxygen level the corrosion products are mainly iron sulphides. As the oxygen level increases, magnetite becomes the major product.

Scale deposition can influence the corrosion of metals. Very often scale deposits accelerate corrosion rate. Iron sulphide deposits can cause severe pitting corrosion. The presence of any type of deposit in water containing hydrogen sulphide, oxygen or carbon dioxide will often increase the severity of any potential corrosion problem.

3. RESULTS AND DISCUSSIONS

3.1 Water Analysis from Felix

Considering the outstanding special therapeutic properties of the geothermal water from Felix Spa this thermomineral water was taken for analysis. Geothermal waters from Felix were analysed in the chemical laboratory from Orkustofnun, Iceland. The results of the laboratory analysis are summarized in Table 1. The wellhead temperature measured during sampling was 42^0C at Felix. As seen from the Table 1, geothermal waters from Felix are slightly basic. The mineralisation of water is very low (Stănăşel et al., 2002). The chloride content is low and the sulphate is higher. The water is carbonated-calcium sulphate type.

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

Component	Well Felix	Component	Well Felix
pH	8	Ca	120.4
CO_2	280.55	F	0.465
B	0.18	Cl	9.8
SiO_2	21.6	SO_4	92
Na	15.44	Al	0.001
K	4.45	Fe	0.013
Mg	19.53	TDS	452

3.2 Corrosion Rates

Corrosion tests were conducted using a set of four metal coupons exposed to fluids from Felix well. The metal coupons used were: carbon steel, stainless steel, cast iron and aluminium. They were exposed for periods ranging between 360 and 2040 hours. The coupons were weighed to 0.001 g accuracy before introducing them into the test. Changes in weight after immersion in the geothermal water were used to determine the effects of corrosion for each kind of coupon (Tables 2 - 5).

$$CR = \frac{\Delta G}{S \cdot t} \cdot \frac{8760}{\rho} \quad (1)$$

where *CR, t, S, ΔG, ρ ,constant* are: corrosion rate in mm/year; exposed time, in hours; exposed area of test material, in m^2; weight loss, in g; test material density, in kg/m^3; 8760, in hours/year, respectively.

Table 2. Material loss and corrosion rate results

Time, hours	Stainless steel	
	ΔG [g]	CR [mm/year]
360	0.0037	0.0025
672	0.0028	0.0010
1440	0.0024	0.0004
2040	0.0019	0.0002

Table 3. Material loss and corrosion rate results

Time, hours	Carbon steel	
	ΔG [g]	CR [mm/year]
360	0.9302	0.640
672	1.4434	0.532
1440	2.6629	0.458
2040	2.817	0.342

Table 4. Material loss and corrosion rate results

Time, hours	Cast iron	
	ΔG [g]	CR [mm/year]
360	0.8343	0.574
672	0.9903	0.365
1440	1.5931	0.274
2040	1.7791	0.216

Table 5. Material loss and corrosion rate results

Time, hours	Aluminium	
	ΔG [g]	CR [mm/year]
360	0.0232	0.0465
672	0.0340	0.0365
1440	0.0603	0.0302
2040	0.0724	0.0256

The data from tables 2 to 5 indicates that the corrosion rate is higher in the first month of testing. The corrosion process decreases then probably due to some corrosion products as iron oxides, which have a little adherence and a high porosity. Experimentally it was noticed a uniform corrosion at the beginning and then a tendency to pitting corrosion.

Corrosion rate varies, depending on the material, the lowest values being recorded for stainless steel, followed by aluminium, cat iron and carbon steel. The recommended material in geothermal installations is stainless steel that has an extremely low corrosion rate, maybe due to a protective layer. An acceleration of the corrosion effect might appear in waters with a high chloride content.

Aluminium even if is less exposed to corrosion attack than cast iron or carbon steel is not recommended for the equipments used in geothermal exploitation, because a significant pitting corrosion has been remarked.

3.3 Scale Analysis from Felix

At Felix solid depositions were observed in the distribution system during utilization. The scale was chemically analysed, the results being summarized in Table 6. The solid sample was XRD analysed by using KαCu radiation. The sample consists mainly in calcite. The amorphous phase has a high Fe content and for this reason an elevated baseline appears on XRD diagram (Figure 1). This is due to the corrosion of the pipe.

Table 6. Chemical composition of the scale deposits from Felix, in %

Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	Calcinated loss
0.3	53	1.2	2.2	0.8	42.4

3.4 Control of Scales by Additives

It was observed that the corrosion process takes place under the calcium carbonate deposits. In order to prevent calcium carbonate scale, tests with inhibitors were made in a low temperature geothermal well from Sudureyri, Iceland. Polyphosphate was used as an inhibitor. There were taken water samples after each dosage of inhibitor. The phosphate and the calcium content were analysed, the first one by chromatography and calcium by atomic absorption spectroscopy at $\lambda = 422.7$ nm. The surface equipments are presented in figure 2 and a few experimental results in table 7. It was found out the minimum dosage of inhibitor that maintains calcium in soluble form, avoiding its precipitation. After two weeks of utilization the additive in the lowest concentration written in Table 7, no carbonate scales were observed.

4. CONCLUSIONS

Taking into account the results of water analysis from Felix, a corrosion process can be estimated, a pH =8 associated with a rather high CO_2 content being a good corrosion supply. The chloride concentration is under 10 ppm, but maybe there are traces of oxygen, which accelerate corrosion. The carbon dioxide content and the calcium concentration of the water can lead to calcium carbonate deposit

According to corrosion rate data you can choose stainless steel for the exploitation equipments of geothermal waters. Carbon steel is very exposed to corrosion, which was also found by the solid deposits formed during utilization. It was proved by chemical and structural analysis that in solid sample iron is in its content due to corrosion, besides the calcite scale.

The tests with additives indicate that a low concentration of inhibitor controls the solid depositions. This leads to an efficient production with little costs as well. The illustrated treatment realised in Iceland in order to avoid calcium carbonate scale could be applied to Romanian geothermal wells, where these depositions have been encountered. A chemical inhibition system is a promising method to combat scaling both technically and economically as compared to mechanical methods.

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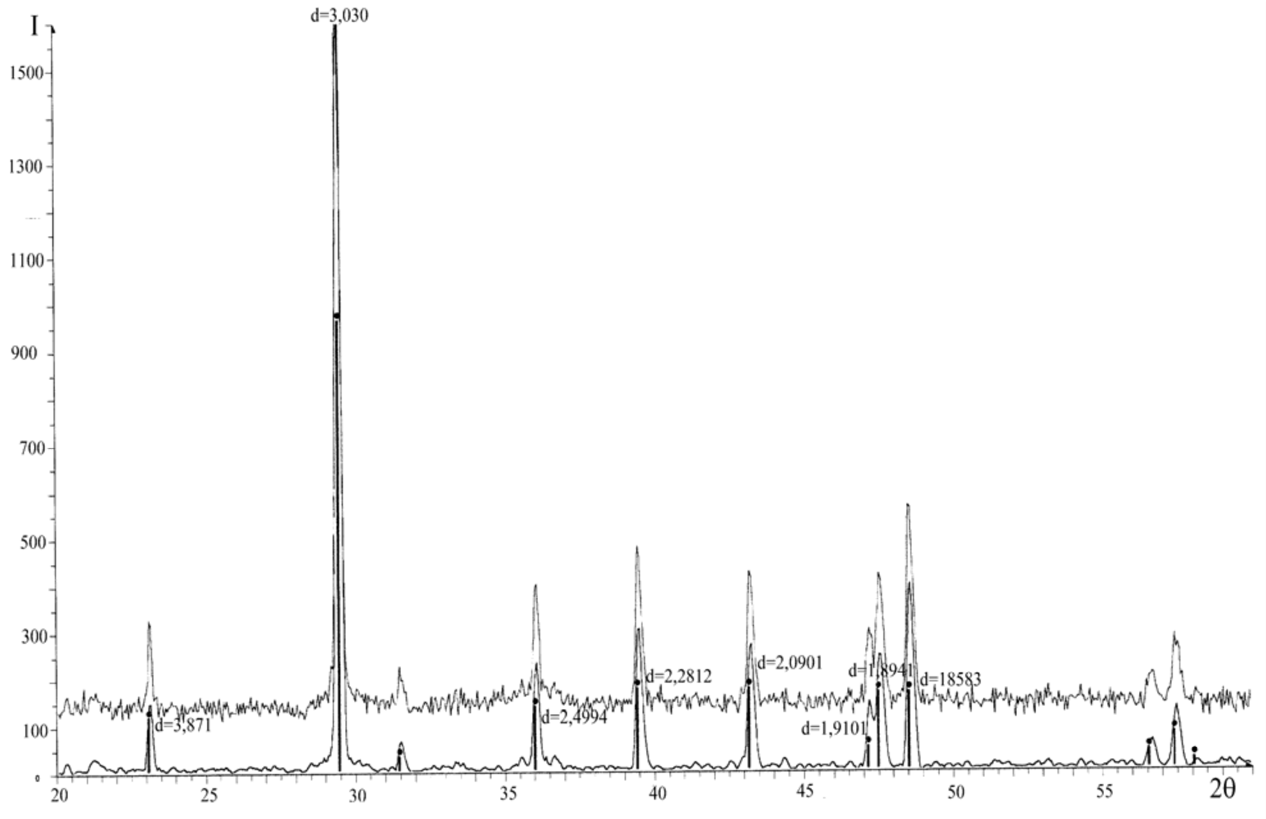

Figure 1: The XRD diagram for depositions from Felix.

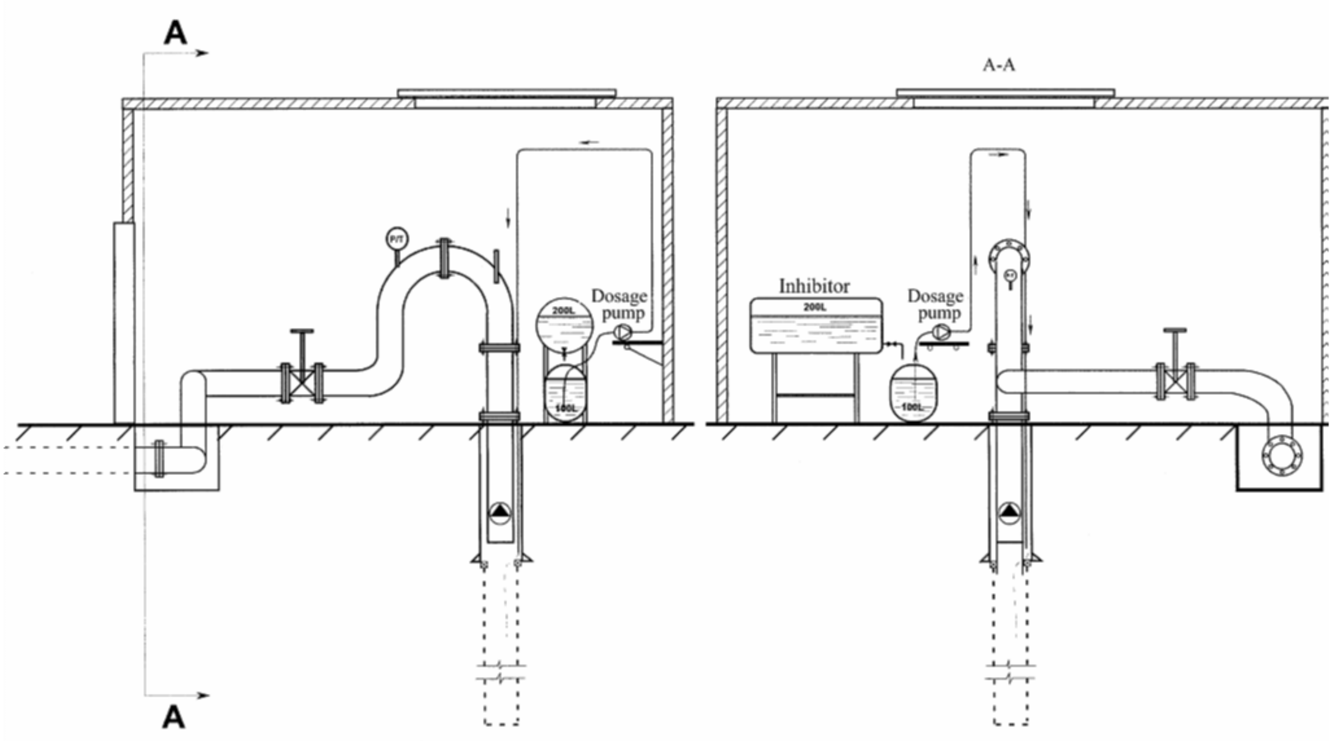

Figure 2: Installation for inhibitor injection

Table 7. Experimental data from Sudureyri

Nr.	Dosage pump		Rate inj.with inhibitor	Flowrate	Inhibitor conc.	Ca^{2+}conc.
	SPM	%Strokes	l/h	l/s	ppm PO_4	ppm
1	40	20	1,14	9,44	0,021	9,7
2	80	60	3,1	9,44	0,322	9,74