IRON CORROSION INHIBITION IN ACIDIC, HIGHLY SALINE GEOTHERMAL WATER

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ABSTRACT

An effective inhibitor of iron corrosion in acidic (pH 3.7), highly saline (ca. 150 g/l) thermal groundwater from West-Lithuania aquifers was found. The inhibition mixture studied consisted of a siliconorganic compound and diethylene ether. Corrosion rates were determined at different inhibitor concentration, solution pH, immersion time, and solution temperature. A degree of protection of up to 90 % was observed when additive concentration reached ca. 0.3 g/l. The corrosion inhibition was predominantly due to the hindering of the anodic half-reaction.

Keywords: iron, corrosion, corrosion inhibitors, thermal groundwater, geothermal fluid.

INTRODUCTION

This paper deals with iron corrosion in geothermal fluids from the West-Lithuanian Geothermal Anomaly (WLGA). The aquifers most suitable for utilization were found here in the Middle/Lower Cambrian geological formation at a depth of 1700-2200 m. The temperature of the geothermal fluids in these aquifers is in the range of 60-95°C, salinity is ca. 150 g/l, and pH is 3.3-3.7. According to classification in /1/, geothermal waters can be divided into ten salinity groups. The highest degree of salinity is when a solution contains over 100 g/l salts. Thus, the fluids from the WLGA are extremely saline.

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The overall corrosive behaviour of iron and carbon steel in geothermal fluids from West-Lithuania was studied previously /2/. Cathodic and anodic Tafel slopes, polarization resistance, and corrosion rates were determined as functions of electrode rotation, immersion time, temperature, and chloride concentration. The oxide layer formed on iron and carbon steel during corrosion was studied by X-ray photoelectron spectroscopy (XPS) using surface sputtering with ionized argon /3/. The thickness of the oxide layer increased with the exposure time in solution and temperature, its values being very similar to aerated, deaerated, and CO_2-saturated solutions. The dynamics of the oxide layer formation was studied by quartz crystal microgravimetry /4/. It was shown that an increase in electrode mass prevailed immediately after the electrode immersion, indicating accumulation of scarcely soluble corrosion products on the surface. The dissolved oxygen favoured formation of the oxide layer in the first corrosion stages.

Due to high salinity and acidity, the West-Lithuanian geothermal fluids are highly aggressive corrosion media. One suitable method of protecting geothermal plant installations is the employment of corrosion inhibitors, which should be injected underground into geothermal fluid. It is commonly known that the efficiency of the inhibitors depends on the physical and chemical properties of the geothermal water, i.e. the salinity, the temperature, the pH, the dissolved gases, etc. Therefore, the efficiency of inhibiting agents may be different in different geothermal aquifers. Indeed, the commercial inhibitors GT-1, GT-2, and Tech-52 are well suited in Romanian geothermal fluids, whereas they have been found to be ineffective under our conditions /5/. Moreover, these substances exhibited an accelerating effect in Lithuanian geothermal waters.

We report in this paper an effective corrosion inhibitor in acid and highly saline geothermal fluid from the West-Lithuanian aquifers. Attention has been also focused on iron corrosion kinetics in the presence of the inhibiting agent.

EXPERIMENTAL

The underground waters were taken out from the *Vidmantai* wells in the Cambrian aquifer and had a temperature of about 80°C. The amounts of dissolved gases (nitrogen, carbon oxide, helium, argon) in the Cambrian brines were in the range of 0.1-1.0 m^3/m^3 /6/. It should be noted that there was no hydrogen sulphide found in the waters, though it is often present in geothermal fluids in other regions.

The content of cations and anions in the geothermal fluid has been determined previously using atomic-absorption spectroscopy, spectrophotometry, and ion chromatography /3/. The results of analysis of the geothermal waters are listed in Table 1.

Table 1
Amount of elements found in the geothermal fluid.

Ion	Amount, g/l
Ca^{++}	22.34
Mg^{++}	4.15
Na^+	16.0
K^+	0.15
Fe^{++}	0.037
NH_4^+	0.11
Cl^-	107.5
SO_4^{2-}	13.7
Br^-	1.2
I^-	1.8
BO_3^{3-}	72.0
	Total salinity 150.4 g/l pH 3.7

Working electrodes were made of pure iron (ARMCO, 99.9). The iron samples with a working area of 1 cm^2 were pressed into Teflon holders. Before each experiment, the surface was abraded with a fine emery paper surfaced with 1-2 μm abrasive particles, degreased with CaO and MgO mixture (weight ratio 1:1), and rinsed with distilled water. The rotating disc electrode was prepared in the same manner. The reference electrode was a saturated Ag/AgCl/KCl electrode.

Cathodic and anodic Tafel slopes (b_c and b_a, respectively) were determined from the steady-state *E-logj* plots obtained by measurements of potentiostatic polarization. The time of establishment of the steady-state current density values during potentiostatic polarization in the cathodic region was approximately 4-8 sec, depending on the polarization value. The stationary current value of anodic dependencies was established in a shorter time (< 4 sec.). In order to determine polarization resistance (R_p) potentiodynamic voltammetric dependencies near to the open circuit potential were recorded. The potential sweep rate was set at 0.1 mV sec^{-1}.

RESULTS AND DISCUSSION

The corrosion current densities (j_c) for iron in the geothermal fluid were determined according to the well-known ratio /7/:

$$j_c = b_a b_c / [2.303 (b_a + b_c) R_p] \qquad (1)$$

The Tafel slopes were ascertained from the steady-state potentiostatic *E-logj* dependencies. The anodic slopes did not vary significantly depending on the immersion time and the electrode rotation frequency and had the values of $b_a \approx$ 80-100 mV. The cathodic slopes were $b_c \approx$ 300 mV for the non-rotated electrode and increased up to $b_c \approx$ 800 mV when electrode rotation n = 1000 rpm was applied. The data on Tafel constants values depending on various factors have been reported in detail in /2,3,5/. Since the condition $b_a << b_c$ is satisfied, the simplified ratio

$$j_c = b_a / 2.303 R_p \qquad (2)$$

may be used instead of eq. (1) for approximate j_c estimations.

The corrosion rates determined according to (1) are shown in Fig. 1. The j_c established in the additive-free solution decreases during corrosion and becomes constant after a certain time. This behaviour may be attributed to the development of surface layer from scarcely soluble corrosion products (the corresponding XPS and EQCM data were considered in /3,4/).

It is commonly known that liquid moves in parallel to the surface of rotating disc electrode (*rde*) in the layers close to it, thus, the geothermal fluid flow in the pipes may be simulated by using *rde*. Obviously, the corrosion current densities are much higher when electrode rotation is applied (Fig. 1). Two depolarizers, viz. proton and dissolved oxygen, may determine the overall corrosion process under the conditions studied. The

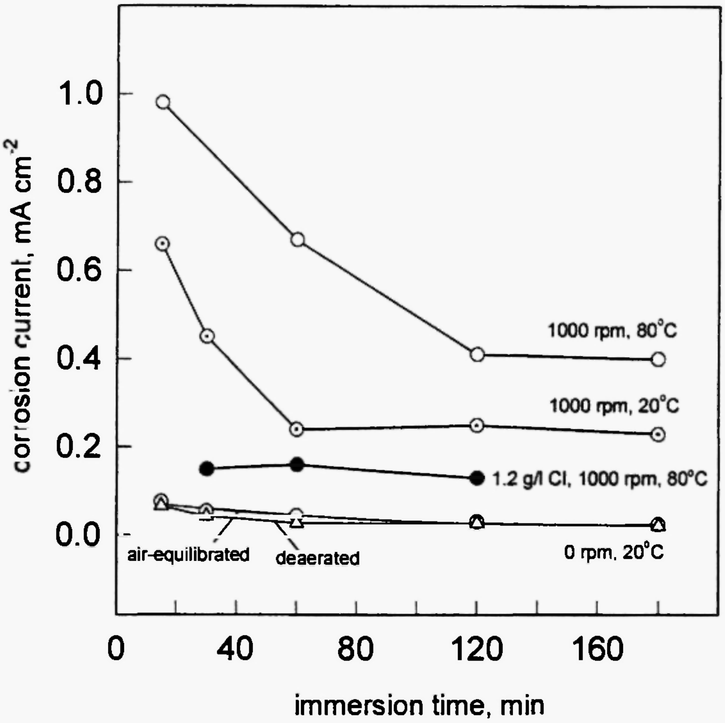

Fig. 1: Iron corrosion rates determined according to eq. (1) in geothermal water.

rise in the corrosion rate on *rde* suggests that reduction of depolarizers takes place as a diffusion limited process.

The corrosion current densities at 80°C, i.e. at the real temperature of the geothermal fluid, are about twice as high as at 20°C (Fig. 1). The temperature effect is more pronounced in the first corrosion stages.

The limiting diffusion current (j_d) was estimated according to Lewich's equation taking into account the concentration of dissolved oxygen and the concentration of free proton /2/. The limiting current for oxygen was found to be $j_{d,O2} = 0.16$ mA cm^{-2} at $n = 1000$ rpm, and the corresponding value for the proton was $j_{d,H+} = 1.36$ mA cm^{-2}. Thus, the corrosion process is due mainly to the proton reduction. The data in Fig. 1 showing that solution deoxygenating causes only a slight decrease in the corrosion rate lead to the same conclusion. The sum $j_{d,O2} + j_{d,H+} = 1.52$ mA cm^{-2} may serve as a rough criterion of the corrosion rate limit at $n = 1000$ rpm in the system studied.

Obviously, the corresponding experimental j_0 values (Fig. 1) are significantly lower. This divergence may be accounted for by the iron surface covering by corrosion products.

The following commonly known iron corrosion inhibitors were tested in the geothermal water under study: polyethylene glycol, polypropylene glycol, butyndiole, urotropine, ethylamine mercaptan, o-phenonthroline, nitrobenzaldehyde, p-nitrobenzoic acid, potassium tartrate, mixtures of butyndiole with boric acid, and tiocarbamide with copper ions. The degree of protection (W) was estimated according to the ratio /8/:

$$W = [(j_0 - j'_0)/j_0] \cdot 100\% \qquad (3)$$

where j'_{cor} is the corrosion current density in the geothermal fluid containing an inhibitor. It was found that all the above substances and compositions were ineffective in the geothermal environment. Moreover, some of them exhibited an accelerating effect (urotropine, p-nitrobenzaldehyde).

The most efficient corrosion inhibitor (CI) was found to be a mixture of two organic substances. The first component belongs to siliconorganic group $(C_2H_5)_2\text{-N-}CH_2\text{-Si}(OC_2H_5)_3$ and the second one is diethylene ether. Neither substances had any inhibition effect separately, and only the mixture of these substances in certain proportions was found to be an effective inhibitor. Fig. 1 demonstrates a significant decrease in corrosion rate in the solution containing 1.2 g/l CI.

The cathodic and anodic voltammograms were obtained in the additive-free geothermal fluid and when CI was added (Fig. 2). These data show clearly that CI inhibition action is due to the hindering of anodic dissolution, whereas cathodic reaction (reduction of H^+ and O_2) remains actually non-affected.

The measurements of an open circuit potential (E_{cor}) lead also to the above conclusion (Fig. 3). The E_{cor} shifts during corrosion to more negative values and reaches a steady state after 1-2 h. The negative shift of E_{cor} implies preferable hindering of the cathodic half-reactions due to the surface covering by oxide layer /3,4/. In the presence of CI, the E_{cor} values are by ca. 50-100 mV more positive than in the additive-free solution. This difference implies that the inhibitor preferably affects the partial anodic reaction.

The inhibition effect depending on additive concentration and immersion time is shown in Fig. 4. A high degree of protection $W \approx$ 80-90% is achieved

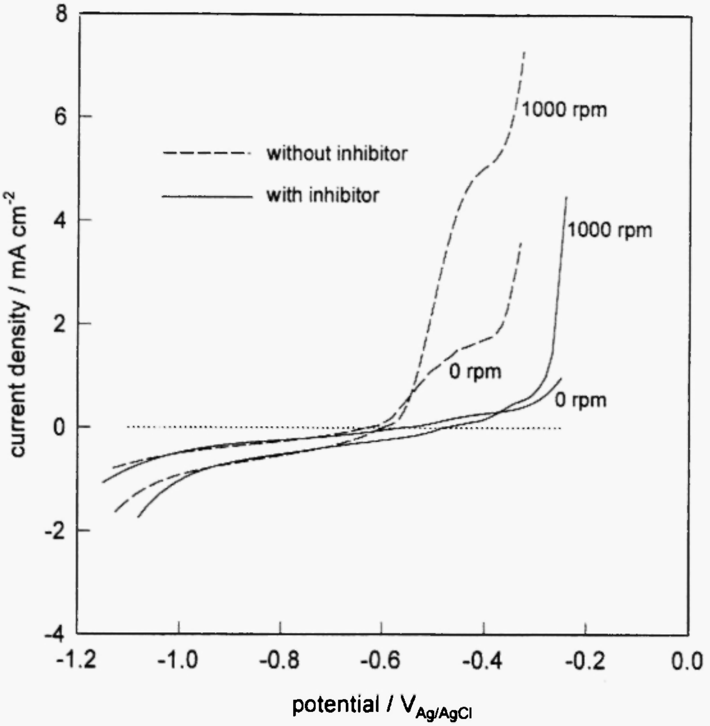

Fig. 2: Voltammograms for iron in geothermal fluid and when 1.2 g/l CI has been added. Immersion time 30 min, solution temperature 20°C.

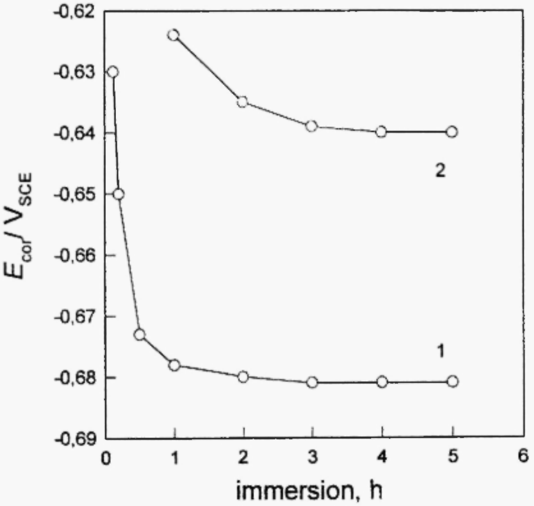

Fig. 3: Open circuit potential *vs* electrode immersion time in geothermal water (1) and when 1.2 g/l CI is added. Solution temperature 20°C.

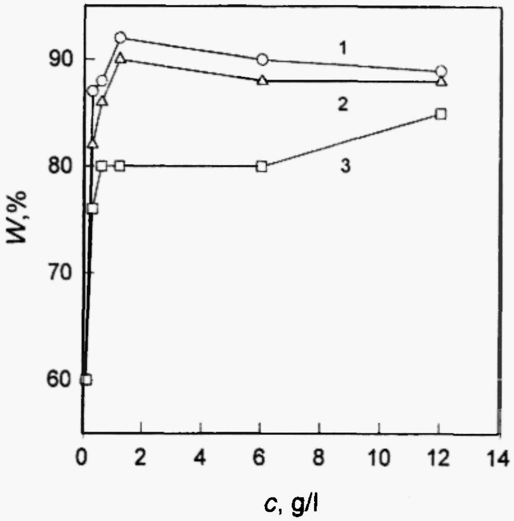

Fig.4: Protection degree *vs* CI concentration. Immersion time (min): 1 -30, 2 - 60, 3 - 120; solution temperature 20°C, electrode rotation 1000 rpm.

at CI concentrations above ca. 0.3 g/l. The degree of protection somewhat decreases with the immersion time. This may be associated with development of oxide layer, which was confirmed by XPS and EQCM measurements /3,4/.

The assumption regarding the reduction of CI inhibiting effect by the oxide layer also supports experiments in solutions of different pH (Fig. 5). The geothermal fluid of pH 3.7 was adjusted to pH 2.8 and 4.8 using HCl and NaOH. While the decrease in *W* during corrosion is observed in all solutions, this effect is especially pronounced in solution of pH 4.8. Obviously, the CI inhibiting properties are mostly suppressed in the solution, where the oxide layer development is mostly favored.

The above data suggest that corrosion rate in CI containing solutions is determined mainly by two factors, viz., CI adsorption and surface covering by oxide layer. The oxide layer plays a negligible part at the beginning of corrosion, because the thickness of the layer is small. In contrast, CI may affect the first corrosion stages significantly due to its adsorption. In the course of corrosion, the oxide layer develops and becomes an important factor, which determines the corrosion rate. Apparently, the CI may be

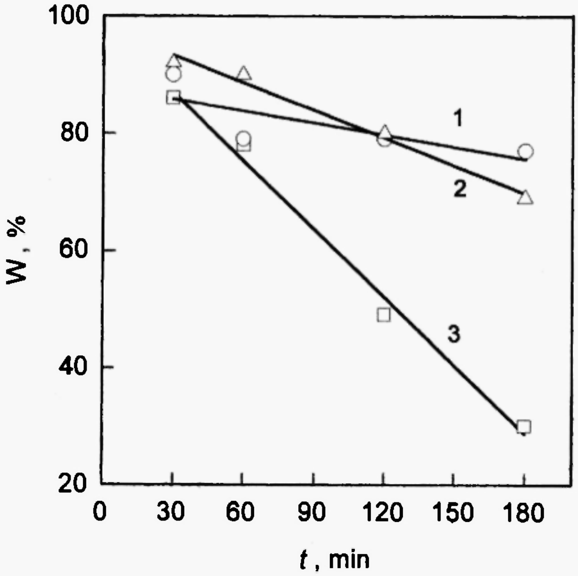

Fig. 5: Protection degree *vs* immersion time in the geothermal solution of pH 3.7 (curve 1) and in the same solution adjusted to pH 2.8 (2) and pH 4,8 (3). Solution temperature 20°C, electrode rotation 1000 rpm, CI concentration 1.2 g/l.

especially effective with respect to surface locations in which the oxide layer is destroyed. CI may effectively reduce the corrosion rate in such damaged locations and significantly prolong exploration of equipment.

CONCLUSIONS

The corrosion behaviour of iron in acidic, highly saline geothermal fluid was studied under laboratory conditions. To simulate hydrodynamic conditions in piping, the rotating disc electrode was used. The limiting diffusion current was estimated according to the Lewich equation taking into account the concentration of dissolved oxygen and the concentration of free proton. These estimations showed that corrosion rate is mainly determined by the proton reduction reaction. Corrosion current measurements in air-equilibrated and in deaerated solutions lead to the same conclusion.

An inhibitor of iron corrosion in geothermal fluid was found. It consisted of a silicon organic compound and diethylene ether. A degree of protection of up to 90% was achieved at an additive concentration of ca. 0.3 g/l. The inhibition action was due to the preferential hindering of anodic half-reaction of the corrosion process.

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