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Variation of carbon steel corrosion rate with flow conditions in the presence of an inhibitive formulation

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Abstract

This work is an extension of studies into the mechanism of inhibition of a carbon steel by a non-toxic multicomponent inhibitor (fatty amines associated with phosphonocarboxylic acid salts) used for the treatment of water in cooling circuits. In a previous work [N. Ochoa, F. Moran, N. Pébère, B. Tribollet, Corros. Sci. 47 (2005) 593], it was shown that the properties of the protective layers formed on the metal surface were dependent on the electrode rotation rate. Moreover, two distinct surface areas were visualised on the metal surface and the ratio between the two zones was dependent on the flow conditions. The present study focuses on the measurement of the corrosion rate from impedance diagrams obtained at the corrosion potential for different electrode rotation rates. The measured polarisation resistances correspond to the anodic process. A non-monotonic variation of the corrosion current densities was observed and explained by the variation of the ratio between the two layers, which each have different intrinsic protective properties. From the polarisation curves plotted in the same conditions, the non-monotonic variation was not shown. Independently of the electrode rotation rate, the corrosion current densities remained low. This study brought an original approach to the influence of flow on the corrosion rate in the presence of inhibitors.

Keywords: A. Mild steel; Electrochemical impedance; Corrosion rate

1. Introduction

Cooling water circuits can present several problems. Corrosion, scale deposit and formation of biofilms can appear when natural waters are used as thermal fluid. These problems can occur jointly, reducing the thermal efficiency of the circuit with significant economic repercussions. To attenuate or eliminate these problems, waters used in cooling circuits are treated with inhibitive formulations composed of corrosion inhibitors associated with chemical reagents added to limit scaling and biofilms.

Today, due to new laws to protect the environment, these compounds must be non-toxic and biodegradable.

In previous studies [1–3], the corrosion inhibition of a carbon steel in a 200 mg L\(^{-1}\) NaCl solution by an original multi-component inhibitor used for treating water in cooling circuits was investigated. The inhibitive formulation was composed of fatty amines (FA) in association with phosphonocarboxylic acid salts (PCAS). It was shown that PCAS act as anodic inhibitors whereas a mixed action was observed for FA. A synergistic effect was observed for the mixture containing 200 mg L\(^{-1}\) PCAS + 50 mg L\(^{-1}\) FA [2]. X-ray photoelectron spectroscopy revealed that the inhibitive film was composed of an iron oxide/hydroxide mixture incorporating the organic molecules. More particularly, PCAS sealed the pores of the oxide layer by forming a chelate [3]. More recently, the inhibition mechanism of
the mixture was investigated by steady-state electrochemical measurements using a rotating disc electrode [1]. It was shown that the formation and the growth of the inhibitive layer were dependent on the electrode rotation rate and on the immersion time. XPS analysis revealed that the higher the rotation rate, the lower the thickness of the inhibitive layer. The thinness of the protective film was explained by the enhancement of the chelate formation by the increase of the electrode rotation rate. Moreover, an original behaviour was observed: two distinct surface areas were visualised on the metal surface after 24 h of immersion in the solution containing the inhibitive mixture. This behaviour was attributed to 'centrifugal force'. A local electrochemical impedance map was plotted above the electrode surface containing the two zones. The map showed that the layer formed at the centre was less protective than that formed at the edge of the electrode [1]. Bommersbach et al. [4,5] recently presented comparable results studying an inhibitive mixture composed of a carboxylic acid and a tertiary amine. They showed that film formation was dependent on the flow conditions [5]. From AFM analyses carried out at different positions on the electrode surface, they showed that film roughness decreases from the centre to the edge of the electrode and thus that erosive action of flow led to the predominance of defects at the periphery of the sample. Finally, in our previous study [1] as well as in the work reported by Bommersbach et al. [4,5], the corrosion rate in the presence of inhibitive mixtures and in the presence of such heterogeneous layers was not determined. Thus, the present work was designed to evaluate the corrosion rate in the presence of the mixture FA + PCAS and to determine the influence of the presence of two layers covering the electrode surface. The corrosion current density was evaluated from the electrochemical impedance diagrams, measured at the corrosion potential for different electrode rotation rates.

2. Experimental

2.1. Materials

Fatty amines and phosphonocarboxylic acid salts were used as corrosion inhibitors. The compounds are presented in Fig. 1. They are current commercial products. Only the mixture with optimised concentrations (200 mg L⁻¹ PCAS + 50 mg L⁻¹ FA), prepared in the laboratory, was studied. This inhibitive formulation, with some other additives, has been patented [6]. The corrosive medium was a 200 mg L⁻¹ NaCl solution (reagent grade) in contact with air maintained at 25 °C. The choice of this medium was based upon the following criteria [7]: (i) its low electrical conductivity is close to that encountered in natural waters, (ii) its corrosivity is fairly high and (iii) it is an easily reproducible baseline solution. The pH of the solution containing the inhibitive mixture was 10.

A rod of XC 35 carbon steel of 1 cm² cross-sectional area was used as working electrode. Its composition in percentage weight was C = 0.35, Mn = 0.65, Si = 0.25, P = 0.035, S = 0.035 and Fe to 100. The microstructure corresponded to ferrite plus fine perlite with some inclusions of MnS. A heat-shrinkable sheath left only the tip of the carbon steel cylinder in contact with the solution. For all experiments, the carbon steel samples were polished with SiC paper down to grade 4000, cleaned in permuted water in an ultrasonic bath and dried in warm air. The counter-electrode was a platinum grid. A saturated calomel electrode (SCE) was used as reference.

2.2. Electrochemical experiments

Polarisation curves were plotted under potentiostatic regulation using a Solartron 1286 electrochemical interface. They were obtained for different electrode rotation rates (Ω). The anodic and the cathodic parts were obtained independently from the corrosion potential at a potential sweep rate of 1 V/h. They were corrected for the ohmic drop, previously determined by electrochemical impedance measurements. The correction level was 80% of the ohmic drop measured at the corrosion potential. Electrochemical impedance measurements were also carried out under potentiostatic regulation using a Solartron 1286 electrochemical interface connected with a Solartron 1250 frequency response analyser. Impedance diagrams were obtained over a frequency range of 65 kHz to a few mHz with six points per decade using a 10 mV peak-to-peak sinusoidal potential. The electrochemical results were obtained from at least three experiments to ensure reproducibility.

3. Experimental results

Fig. 2 shows, as an example, the polarization curves obtained for three electrode rotation rates in the 200 mg L⁻¹ NaCl containing the inhibitive mixture. When the electrode rotation rate increased, the cathodic current densities increased, the anodic current densities decreased and the corrosion potential became shifted in the anodic direction. In Ref. [1], it was shown, from the polarisation curves, that the cathodic process is not modified in the presence of the inhibitive mixture (the cathodic plots are identical in the presence and in the absence of the inhibitive mixture) and is classically controlled by oxygen diffusion.
Thus, the increase of the cathodic current densities with the electrode rotation rate is explained by an increase of the oxygen supply to the metal surface. The decrease of the anodic current density when the electrode rotation rate was increased is an unusual behaviour previously explained by the morphology and the chemical composition of the inhibitive layers [1]. In the present study, photographs of the electrode surface were taken for different electrode rotation rates after 2 h of immersion in the solution containing the inhibitive mixture (Fig. 3). In contrast to our previous study [1], where the electrode surface appeared bright after 2 h of immersion, in the present study the two distinct areas were clearly visualised on the metal surface. For 400 rpm, a whitish layer covered the whole electrode surface. For the three other rotation rates, the surface area covered by the whitish layer decreased as the rotation rate increased. By 2000 rpm, only a very small circular spot was observed. On the edge, the electrode surface appeared bright. The same phenomenology was previously observed after 24 h of immersion and attributed to a mechanical effect linked to ‘centrifugal force’ and not to a current or a potential distribution because the same phenomenon was observed on an electrode of twice the radius [3].

Inspection of the photographs in Fig. 3 reveals that the whitish layer is not homogeneous and thus localized corrosion was able to occur under this layer. However, when the electrode surface was washed with alcohol, the whitish layer disappeared and the surface was seen to be perfectly bright without pits. This shows that the corrosion rate in the presence of the inhibitor is low and that there is no localized corrosion.

From the polarisation curves, it is usual to determine the corrosion current density, $I_{\text{corr}}$, by extrapolation of the anodic and cathodic curves. In the present case, the cathodic process is mass transport controlled and independent of the presence of the inhibitive mixture. Thus, $I_{\text{corr}}$ cannot be extracted from the cathodic branch. From the anodic branch, the estimation of $I_{\text{corr}}$ is not accurate. According to the electrode rotation rates, $I_{\text{corr}}$ varies between a few $\mu$A cm$^{-2}$ to less than 20 $\mu$A cm$^{-2}$ (Fig. 2). Due to this lack of accuracy, the corrosion current determination was not reported in our previous work. To obtain an accurate measurement of $I_{\text{corr}}$, the study was pursued using electrochemical impedance spectroscopy. The impedance diagrams were recorded separately after 2 h of immersion at the corrosion potential for different electrode rotation rates to measure the corrosion current. Fig. 4 shows, as an example, the impedance diagrams obtained for the four electrode rotation rates.

![Fig. 2. Polarisation curves obtained for the carbon steel electrode for three electrode rotation rates after 2 h of immersion at $E_{\text{corr}}$ in the 200 mg L$^{-1}$ NaCl solution containing the inhibitive mixture (200 mg L$^{-1}$ PCAS + 50 mg L$^{-1}$ FA): (■) 100 rpm, (□) 1000 rpm, (●) 2000 rpm.](image)

![Fig. 3. Photographs of the electrode surface obtained after 2 h of immersion in the 200 mg L$^{-1}$ NaCl solution containing the inhibitive mixture: (a) 400 rpm, (b) 1000 rpm, (c) 1600 rpm, (d) 2000 rpm.](image)
electrode rotation rates corresponding to the photographs reported in Fig. 3. The diagrams are characterised by a single capacitive loop. It can be observed that the value of the polarisation resistance significantly increased between 400 rpm and 1000 rpm and then decreased between 1000 rpm and 1600 rpm and continued to decrease between 1600 rpm and 2000 rpm. The impedance diagrams can be fitted by a simple equivalent circuit composed of the electrolyte resistance, $R_e$, in series with the polarisation resistance, $R_p$, in parallel with a capacitance, $C_d$. The capacitances were replaced by constant phase elements (CPE) to take into account the non-ideal behaviour of the interface [8–10].

The CPE is given by

$$Z_{CPE} = \frac{1}{Q(j\omega)^\alpha}$$

where $\alpha$ (CPE exponent) is related to the angle of rotation of a purely capacitive line on the complex plane plots and $\alpha$ is generally close to 1.

The values of the parameters, obtained from the fit, are reported in Table 1. It can be seen a non-monotonic variation of $R_p$ which decreased, increased and again decreased when the electrode rotation rate varied from 100 rpm to 2000 rpm. Conversely, the value of $Q$ and $\alpha$ appeared relatively constant independently of the electrode rotation rate and thus independently of the presence of the two layers on the electrode surface. The $\alpha$ value, between 0.8 and 0.9, can be attributed to the time constant distribution in the 2 or 3 dimensions or both [10]. The values of $Q$ are in the range of a double layer capacitance for a totally active surface, which is in agreement with the cathodic behaviour.

As previously mentioned, the cathodic current is controlled by mass transport. Thus, at the corrosion potential, the corresponding faradaic impedance in the low-frequency range is very high with respect to the anodic impedance. As a consequence, the polarisation resistance ($R_p$), reported in Table 1, essentially corresponds to the anodic charge transfer resistance ($R_{ta}$). Finally, from the $R_p$ values given in Table 1, the corrosion current densities ($I_{corr}$) were estimated, for each electrode rotation rate, by using the simplified Stern and Geary relationship [11]:

$$I_{corr} = \frac{b_i}{2.3R_p}$$

where $b_i$ is the exchange current density. The slope of the curves in the anodic range was measured from Fig. 2 and estimated at 300 mV/dec. The variation of $I_{corr}$ as a function of the square root of the electrode rotation rate is reported in Fig. 5. It must be noted that the corrosion current densities remain low independently of the electrode rotation rate. However, a non-monotonic variation of the corrosion current density is clearly observed in agreement with the non-monotonic variation of the polarisation resistance.

The results can be analysed by using a schematic representation of the cathodic and anodic parts of the system as illustrated in Fig. 6. When the electrode rotation rate increased, the cathodic current densities increased. For an infinite rotation rate, the cathodic curves would be shifted to infinity. On the contrary, the anodic current densities decreased when the electrode rotation rate increased. This variation of the anodic current versus the rotation rate is limited by the presence of the two layers on the electrode surface, and, thus, two limiting cases are reported in continuous lines in Fig. 6: (i) for the lowest rotation rate, when the electrode surface is totally covered by the whitish layer and (ii) for...
The corrosion current densities ($I_{corr}$) monotonically decrease as a function of the electrode rotation rate. Fig. 7. Schematic representation of the variation of the corrosion current densities, which remain low. The experimental results reported in Fig. 5 are in agreement with the schematic representation given in Fig. 7.

At low rotation rates, the corrosion current densities are low even if the whitish layer is poorly protective. At high rotation rates, the corrosion current densities are of the same order of magnitude due to the fact that the layer is more protective. Between these two domains, the protective properties of the two layers control the corrosion current densities, which remain low. The experimental results obtained at $E_{corr}$ in the presence of the inhibitive mixture, underlined that the protective properties of the layers were dependent on the electrode rotation rate at which the layers were formed. In other words, the impedance diagrams reported in Fig. 4 account for the variation of the surface area covered by the two layers and also for the intrinsic properties of the inhibitor films brought about by the electrode rotation rate.

4. Conclusion

The variation of the carbon steel corrosion rate in the presence of an inhibitive mixture composed of fatty amines (FA) and phosphonocarboxylic acid salts (PCAS) was evaluated from impedance data and polarisation curves for different electrode rotation rates. It was shown from the impedance results that the variation of $I_{corr}$ was non-monotonic. This behaviour was explained by taking into account both the steady-state results and the presence of the two layers on the electrode surface and was attributed to the variation of the surface area covered by the two layers. This study stresses the necessity for careful analysis of the data before attempting to interpret the impedance diagrams or evaluate the corrosion rate. This work will be pursued studying the influence of the immersion time on the corrosion rate for different electrode rotation rates. A similar study with only the PCAS compound could be considered because it was seen [2] that PCAS only has an anodic action and thus it might be responsible for the variation observed in $I_{corr}$.

References