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Corrosion inhibition of carbon steel in alkaline chloride media by Na_3PO_4

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Abstract

The decrease of the pH of the concrete due to the interaction with the CO_2 contained in the air creates an electrolyte in the pores with a pH < 8 that destroys the passive film. Also the presence of chloride ions at the rebar surface in alkaline media making susceptible to the aggression of the chlorides as pollutant in marine environment. The inhibiting efficiency of Na_3PO_4 against corrosion of carbon steel in alkaline medium simulating the interstitial solution of the concrete (pH 12.5) polluted with chloride ions were carried out. Two manners for adding the Na_3PO_4 were examined: one where the inhibitor was added into the pore solution also containing the aggressive solution, and other where the rebar was first pre-treated by immersion in the inhibitor solution. The protective effectiveness of these two procedures for the inhibitor addition was evaluated by means of several electrochemical techniques, EIS, polarisation curves and microbalance.

The results allow concluding that:

- The pre-passivation procedure is more effective for the rebar protection.
- The impregnation duration of steel in phosphate solution and the electrode rotation speed influence considerably the phosphate-based film resistance against corrosion.

1. Introduction

The corrosion of steel rebar constitutes one of the main causes of the degradation of reinforced concrete structures. The two main sources of corrosion are the presence of carbon dioxide and chloride ions. Carbon dioxide present in the air penetrates into the pores of the concrete and reacts with the alkaline compounds leading to pH decrease and consequent loss of passivation of the rebar. Also the steel surface of the rebar becomes sensitive to the chloride ions even in the alkaline media of the concrete, which induce local depassivation of the rebar's leading to pitting corrosion. In order to protect the steel against corrosion several palliatives of procedures are proposed in the literature, those are: (1) galvanized reinforcement, (2) steels, stainless steel rebar,

(3) CP cathodic protection, and (4) corrosion inhibitors. The last method was envisaged as an interesting solution, because it is easy to apply with reasonable additional cost [1], several studies were devoted to this rebar protection system [2–5]. This study has been focussed in corrosion inhibitors that are in contact with the steel before casting the concrete or added in the mix simultaneously with the aggressive.

The use of sodium monofluorphosphate (Na_2PO_3F) was proposed to decrease the corrosion rate of reinforcement in the presence of chloride [6] and in the presence of carbonation [7–9]. However, its effectiveness in concrete is controversial and varies with the method of application to the concrete.

In previous works, it was shown that sodium phosphate (Na_3PO_4) inhibits pitting corrosion of steel in simulated pore solution if its concentration is higher than the chloride one [10]. However, its efficiency is partially lost if this compound is added directly into concrete [11].

Previous investigations [12] show that the pre-treatment of steel rebar's reveals inhibiting properties delaying the initiation

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of corrosion. The rebar's immersion during 7 days in Na_3PO_4 (0.5 M) favors the formation of a passive layer on the steel rebar surface, able to resist for longer periods the action of chlorides that initiate corrosion. The stability of this passive layer seems to depend on the immersion time in the phosphate solution.

In this work, the effect of the hydrodynamics conditions, using a rotating electrode, is examined on the formation of inhibitor passive layer, and its protective performance against the corrosion in alkaline medium simulating the interstitial solution of the concrete (pH 12.5 in this case) contaminated by chloride ions is evaluated.

2. Experimental conditions

The procedure for the preparation of working electrode will be described first, then the electrolyte used in the present corrosion test, and finally the experimental devices used in the present investigation will be presented.

2.1. Working electrode

The working electrode was made of a carbon steel rod of 5 mm in diameter embedded into an epoxy resin to form a disk electrode. A cataphoretic paint (PPG; W788 I 323 + W975 G 323) was applied beforehand on the lateral part to avoid an infiltration of the electrolyte. So the electrode surface was only the cross-section, and equal to $0.2 \, cm^2$. Two electrode rotation speeds were used: 100 and 500 rpm. For measurements in quiescent solution, the electrode rotation rate was zero. Just before each experiment, the electrode surface was abraded by emery-paper up to 1200 grade; then rinsed with doubly ion-exchanged water. After polishing, the electrode was transferred to the electrochemical cell as soon as possible to minimize oxidation with the air.

2.2. Electrolytes

The electrochemical tests were carried out in different solutions, at the room temperature ($25 \pm 5 \, °C$) without stirring.

2.2.1. Corrosion test solution: blank solution—S_1

A $Ca(OH)_2$ saturated solution contaminated by chloride ions by addition of 0.5 M NaCl was used as the blank test solution (S_1). This solution simulates the interstitial liquid of the concrete immersed in seawater.

2.2.2. Solution with added inhibitor—S_2

The solution with the inhibitor was prepared in parallel with the blank solution in which it was added together with the chlorides, $0.5 \, M \, Na_3PO_4$ (S_2).

2.2.3. Pre-treatment of rebar with inhibitor

Pre-treatments of steel rebar were carried out in 0.5 M Na_3PO_4; the steel electrode was immersed during 2 and 72 h in this solution to form a protective layer. Later the pre-treated rebar was immersed in the blank solution containing chlorides (S_1).

2.3. Electrochemical measurements

Electrochemical impedance spectroscopy and polarisation measurements were carried out by means of a potentiostat (Gamry, model PC4/300). The electrochemical impedance spectroscopy (EIS) was measured with frequency ranged between 100 kHz and 10 mHz, using a 10 mV (rms) sinusoidal potential perturbation. The EIS were collected at the open-circuit potential determined just before launching the experiments. Before any impedance measurement and unless otherwise indicated, the electrode was held during 2 h at the open-circuit corrosion potential. Measurements at 2 and 72 h were carried out.

The polarisation curves were made at a sweep-rate of 1 mV/s, from the E_{corr} potential to the cathodic direction.

For electrochemical quartz crystal microbalance (EQCM) experiments, the iron was vapour deposited on a quartz crystal blade (6 MHz AT-cut) upon which a thin gold layer has been vacuum deposited previously. The surface area of EQCM electrode was $0.22 \, cm^2$. The quartz crystal electrode was fixed with electrical conducting glue on a circuitry board made of a glass-fibre reinforced epoxy resin. The iron deposited surface was set outside, and a silicon sealant (Sodiema, Aracolle) allowed avoiding the solution leakage to the backside of the quartz blade.

For the gravimetric measurements, the results are presented as the mass variation with respect to time. The mass changes were derived from the observed frequency changes using the Sauerbrey equation [13]:

$$\Delta f = -K_s \Delta m \tag{1}$$

where Δf is the frequency change, Δm mass change and K_s the constant depending upon the resonant frequency of the quartz, in this case, the nominal frequency was 6 MHz. K_s was determined experimentally by means of the electrodeposition of iron according to Faraday law [14], and was equal to $52 \, Hz \, \mu g^{-1} \, cm^2$.

3. Results and discussion

3.1. EIS study in quiescent solution

Fig. 1A–C shows the impedance diagrams of a steel electrode immersed in all systems (steel electrode/S_1 solution, steel electrode/S_2 solution and pre-treated steel electrode/S_1 solution), during 2 and 72 h in quiescent solution (electrode rotation rate = 0 rpm).

When the steel electrode is immersed in the blank solution (S_1), the impedance spectra's are formed by two capacitive loops (Fig. 1A). One at the high frequency range and the other loop at the low frequency range. This last shows an asymmetrical form can be seen. This can be attributed to a diffusion impedance process with a finite thickness of diffusion layer.

An equivalent electric circuit with three time constants has been tried to reproduce these results. Though, only two capacitive loops are clearly visible but on asymmetrical, the circuit illustrated in Fig. 2 is the simplest one to carry out a parameter regression calculation by a simplex method sufficiently close to the experimental data.
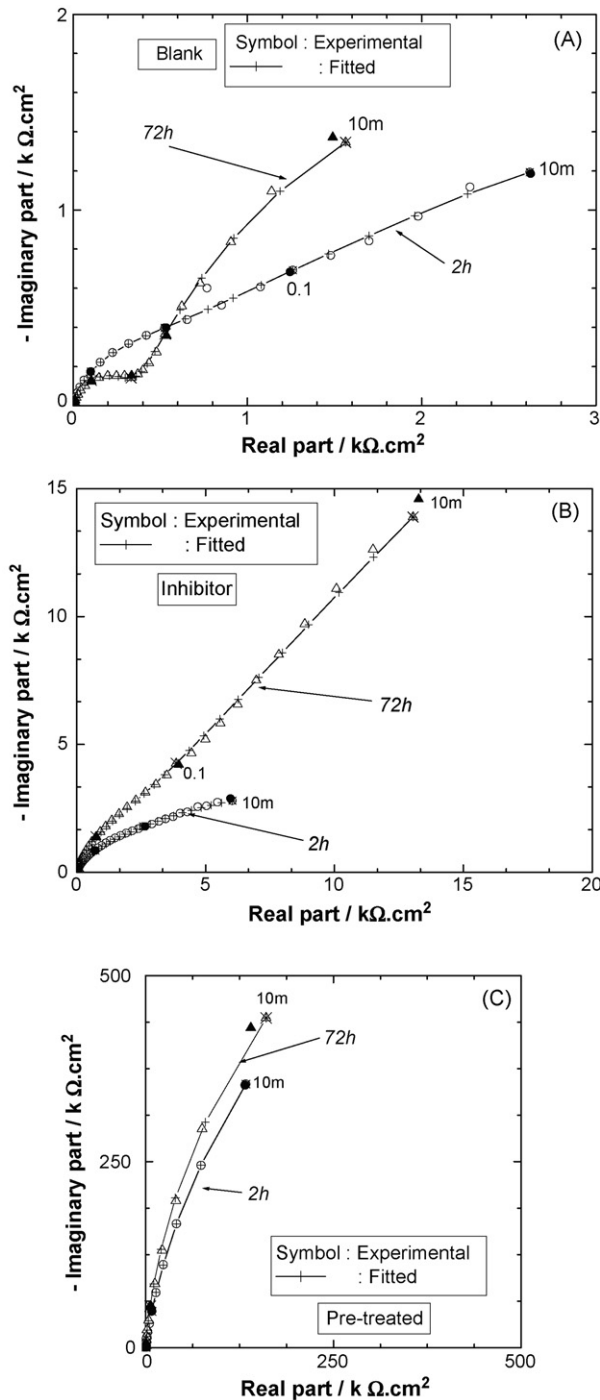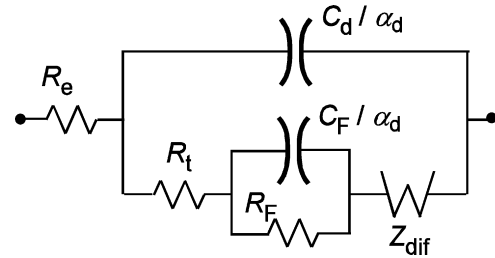
Fig. 2. Equivalent electric circuit reproducing the results presented in Figs. 1 and 3.

the charge transfer resistance is the response of the electrode interface with a high frequency perturbing signal such that the concentration of the reacting species at the electrode surface cannot follow the potential change. In contrast, the faradaic resistance represents the response of the system when the ac frequency of perturbing signal is low enough that the surface concentration follows completely the relaxation phenomenon.

Fig. 1B represents the impedance spectra of steel electrode immersed in S_2 solution, it appears that the low frequency limit of the impedance is at least one order of magnitude greater than that observed in the blank test solution. Thus, the decrease of the corrosion current is expected, and the diffusion process may no longer intervene into the corrosion kinetics. This hypothesis is supported by the fact that the low frequencies branch is definitely greater than 45°. Consequently, we will use the equivalent electric circuit presented in Fig. 2 but without the diffusion element.

Fig. 1C presents the impedance spectra of pre-treated carbon steel during 2 or 72 h in Na_3PO_4, and then immersed during 2 h in the corrosion test solution. The low frequency limit of the impedance is again about one order of magnitude greater than those observed in the inhibitor containing medium, thus two or three orders of magnitude greater than those collected in the blank test solution. All diagrams are exhibited only one capacitive loop. Therefore, the regression calculation was performed with an equivalent electric circuit involving only one time-constant ($R_e - (R_t - C_d)$).

The impedance spectra are then analysed with a non-linear regression calculation with a simplex algorithm. The calculation results are presented in Table 1.

In all cases, the high frequency limit of the measured impedances is close to $5\,\Omega\,cm^2$. This resistance corresponds well to that due to the finite conductivity of the medium, that is, the electrolyte resistance. The values of α_d and α_F are located between 0.8 and 0.9, the values frequently reported on a solid electrode, and reveal heterogeneity of the steel surface.

The C_d values are between 30 and 100 $\mu F\,cm^2$, these values suggest that the reason of this capacitance could reasonably be attributed to the double layer with the passive film. It can be noticed that the capacitance decreases with the immersion time, which corresponds to the modification of passive film towards more organized structure with a loss of charge career.

From this table, it clearly appears that the R_t values increase according to the following order: "blank < inhibitor < pre-treatment". The pre-treatment of carbon steel will be therefore

Fig. 1. Impedance diagrams (Nyquist representation) of (A) steel electrode/S_1 solution, (B) steel electrode/S_2 solution and (C) pre-treated steel electrode/S_1 solution; after 2 and 72 h of immersion.

In this circuit, each element is attributed, in agreement with the values obtained of the parameter regression calculation. R_e: electrolyte resistance, R_t: charge transfer resistance, R_F: faradaic resistance associated likely to the oxidation–reduction process between Fe(II) ↔ Fe(III) in the passive layer, C_d: double layer capacitance, C_F: faradaic capacitance. α_d and α_F: coefficients allowing representing the depressed shape in the Nyquist diagram, Z_{diff}: diffusion impedance. It will be worth to recall that

Table 1
The results of non-linear regression for the impedance spectra presented in Fig. 1

System	Time (h)	R_e (Ω cm^2)	R_t (kΩ cm^2)	C_d (μF cm^{-2})	R_F (kΩ cm^2)	C_F (mF cm^{-2})	R_d (kΩ cm^2)	T_d (s)	E' (%)
Steel/S$_1$ solution	2	4.85	0.35	80.32	3.56	10	1.65	14.80	–
	72	4.91	0.31	74.43	3	20	1.87	22.74	–
Steel/S$_2$ solution	2	5.02	0.5	84.29	268	5.78	–	–	38
	72	4.99	3.22	61.56	18.32	4.91	–	–	89.13
Pre-treated steel/S$_1$ solution	2	4.89	1335	40.28	–	–	–	–	99.97
	72	4.79	1776	34.10	–	–	–	–	99.98

the most effective method to protect against the corrosion. From R_t value, the inhibiting efficiency (E') was calculated according to the following equation:

$$E' = 100 \times \frac{R_t - R_t^0}{R_t} \qquad (2)$$

For the pre-treated carbon steel, the protective effectiveness exceeds 99.9%. Compared with the untreated carbon steel immersed in S$_2$ solution, it was observed that effect of Na$_3$PO$_4$ is enhanced, and the corrosion current becomes smaller.

The faradaic resistance R_F increases in the same order than the charge transfer resistance. As this resistance is to be associated with the stability of the passive film, it can be concluded that the passive film obtained in presence of the inhibitor is quite stable. On the other hand, the effect of the immersion time is not significantly affecting this response. The value of C_F is compatible with the hypothesis on the origin of this loop attributed to an oxidation–reduction process involving corrosion products.

The diffusion constant time, τ_d increases for 72 h immersion, however, the R_d is slightly affected.

3.2. EIS study with RDE

The same experiments were carried with two electrode rotation speeds ($\Omega = 100$ and 500 rpm) (Fig. 3).

With blank specimens (Fig. 3A), the Nyquist diagrams are modelled by the same equivalent electric circuit shown in Fig. 2. A systematic error was observed in the intermediate frequency domain, and the divergence between experimental and calculated data is markedly higher than that expected by the scattering of experimental data evaluated arbitrary to be less than 1% of the impedance modulus. The fitting is particularly poor for the lowest Ω values (100 rpm), but could be considered as adequate for the highest Ω values (500 rpm). This can be explained by the fact that the bounded diffusion approximation in solution starts to be valid only for high Ω values [15].

As can be expected, the impedance modulus, of the steel electrode immersed in S$_2$ solution, increased dramatically with the immersion time and the rotation speed (Fig. 3B). However, no marked effect of immersion time and rotation speed is noted in the case of pre-treated carbon steel (Fig. 3C). It seems that the rotation speed helps to the formation of a passive layer when the inhibitor is added in solution (S$_2$). The impedance spectra's for system steel/S$_2$ solution were modelled with the same equivalent electric circuit presented in Fig. 2 but without the diffusion

element. As for the system pre-treated steel/S$_1$ solution, we used the same circuit that for the quiescent solution ($R_e - (R_t - C_d)$).

Table 2 displays the variation of protective effect of Na$_3$PO$_4$ with respect to time for the rotation speed equal to 100 and 500 rpm.

It is remarked also that the inhibiting efficiency is not significantly affected with rotation speed.

In the whole cases (Table 2), the protective effectiveness is important. Furthermore, the inhibiting efficiency tends to increase with the pre-treated carbon steel.

3.3. Cathodic polarisation curves

Fig. 4 illustrates the cathodic polarisation curves of untreated and pre-treated carbon steel immersed in the blank solution (S$_1$). These curves were obtained after a preliminary stabilisation period of 2 h on the open-circuit potential at various electrode rotation speeds.

For the untreated carbon steel (Fig. 4a), it was observed that the cathodic currents exhibit a diffusion limiting plateau between -0.8 and -1.1 V depending on the electrode rotation speed, the cathodic polarisation curves were controlled by the mass transport in these potential domain [16]. This limiting current corresponds to the reduction of dissolved oxygen.

In the case of pre-treated carbon steel (Fig. 4b), the current plateau was observed, but the cathodic polarisation curves are no longer determined by the disk rotation speed. The limiting current observed is ca. 10 μA cm^{-2} corresponding to a thin passive layer trough which the diffusion process is taking place.

3.4. Gravimetric measurements

According to the previous results, in this part it was studied only the pre-treated carbon steel/S$_1$ solution. Fig. 5 presents the variation of the mass and the potential of carbon steel treated during 24 h in 0.5 M Na$_3$PO$_4$ solution, then immersed in S$_1$ solution.

It appears that the corrosion potential increases during the pre-treatment period indicating a growing of the passive film on the rebar surface. The mass of products formed on the interface increases with time revealing an improvement of the film formed on the steel surface. When it was changed the phosphate solution by the aggressive medium, it was noticed that the mass decreased steeply with a value around 3 μg cm^{-2}, beyond this period, the mass no longer change and becomes stable with time.
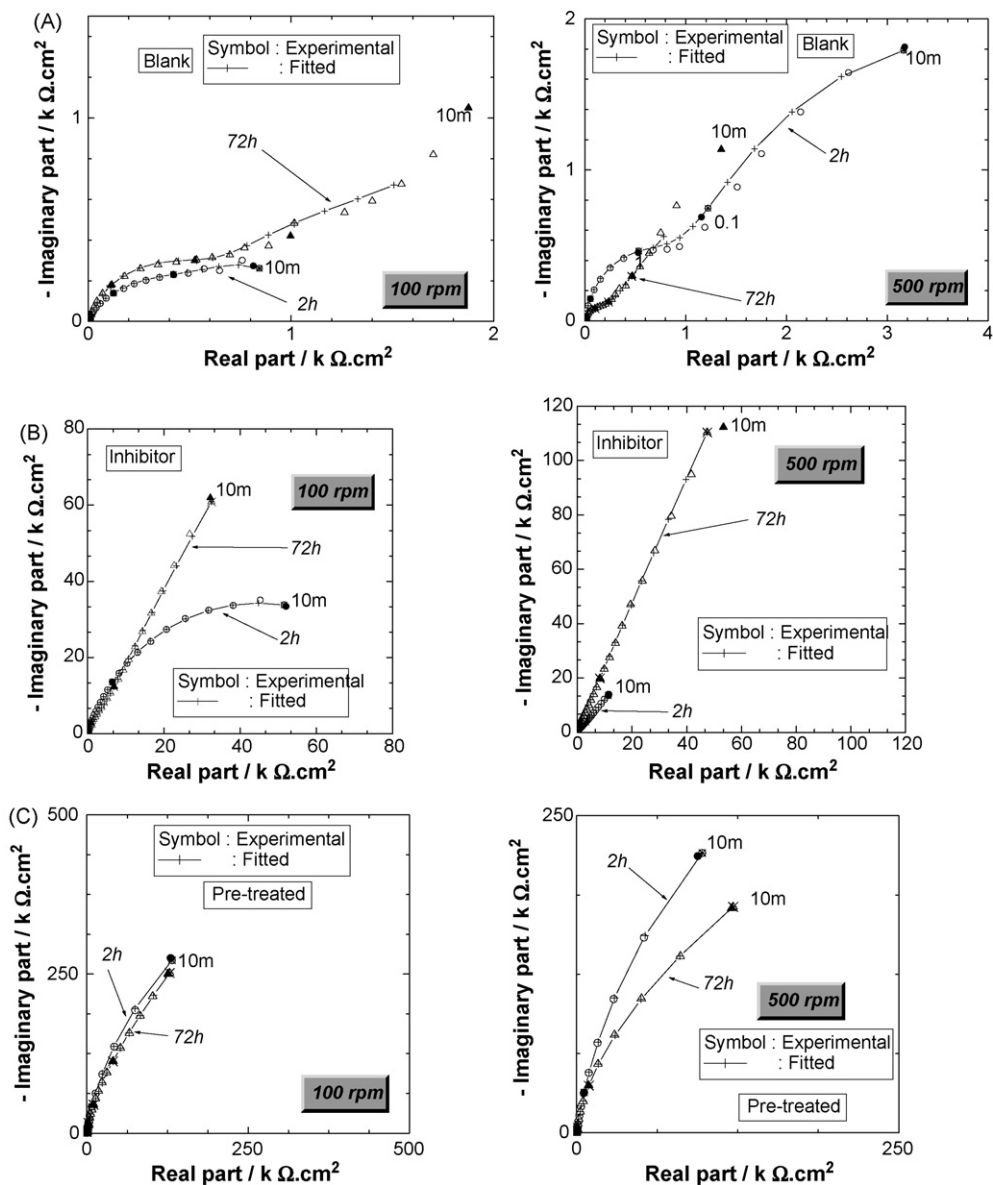
Fig. 3. Impedance diagrams (Nyquist representation) of (A) steel electrode/S_1 solution, (B) steel electrode/S_2 solution and (C) pre-treated steel electrode/S_1 solution; for two periods of immersion: 2 and 72 h and for two electrode rotation rate values: 100 and 500 rpm.

Table 2
R_t and C_d changes with respect to immersion period in the all systems for $\Omega = 100$ and 500 rpm

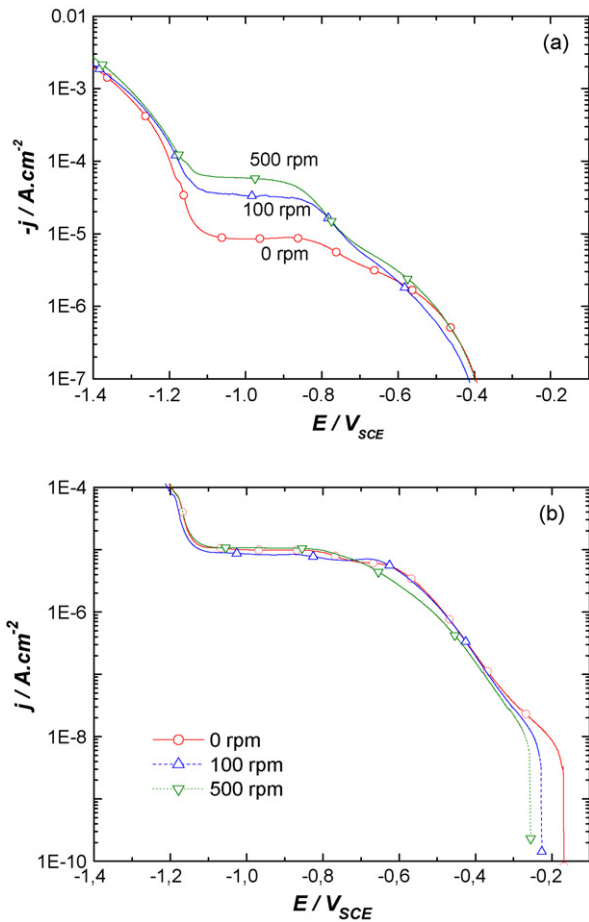| System	Ω (rpm)	Time (h)	R_t (kΩ cm^2)	C_d (μF cm^{-2})	E' (%)
Steel/S_1 solution	100	2	0.096	88.22	–
		72	0.663	79.82	–
	500	2	0.862	72.68	–
		72	0.146	61.62	–
Steel/S_2 solution	100	2	10.036	62.94	99.04
		72	8.696	49.61	92.37
	500	2	2.350	102.56	63.32
		72	9.689	36.42	98.49
Pre-treated steel/S_1 solution	100	2	528	45.77	99.98
		72	610	41.45	99.89
	500	2	482	49.47	99.82
		72	395	50	99.96

Fig. 4. Cathodic polarisation curves of the (a) untreated and (b) treated carbon steel (immersed during 72 h in 0.5 M Na₃PO₄) and then immersed in the corrosion test solution.

These results are in agreement of a sample correctly protected against the aggression of chlorides ions. Indeed, the corrosion process, therefore amount of steel dissolution should lead to a mass decrease. If the mass increase observed is due to (OH) molecules and not to iron dissolved from the electrode surface,

and considering the specific density of Fe(OH)$_3$ as 3, then the thickness of the passive layer calculated after 24 h of immersion period is around 0.1 μm. If this thickness is used to evaluate the diffusion coefficient by using the Fick's first law, the value obtained is $D \approx 10^{-9} \, \text{cm}^2 \, \text{s}^{-1}$. This D value is reasonable for a diffusion process through the solid the passive layer. It can be roughly approach that the passive film thickness obtained in Na$_3$PO$_4$ is in the order of 0.1 μm.

4. Conclusion

The results obtained in this work clearly show that the pre-treatment test reveals good inhibiting properties. The pre-treatment helps to the formation of a protective layer on the surface that prevents the access of aggressive anions to the steel interface. Moreover, the impedance results show that this layer becomes more resistant with time. Also, it shows that the charge transfer resistance R_t, closely related to the corrosion rate, increase according to the following order: "blank < inhibitor < pre-treatment". The pre-treatment of carbon steel will be the most effective method to protect against the corrosion. The inhibiting efficiency (E') evaluated from R_t value exceeds 99%.

Polarisation curves show that for the untreated carbon steel, the cathodic curves were controlled by the mass transport of dissolved oxygen through the electrolyte at the vicinity of the electrode surface. In contrast, in the case of pre-treated carbon steel, the diffusion plateau is no longer dependent on the rotation speed of the disk electrode. The diffusion may likely takes place through the oxide layer.

Gravimetric measurements obtained by electrochemical quartz crystal microbalance (EQCM) show that the mass of the products formed at the interface increases with time revealing a thickening of the film formed on the steel surface. The thickness of oxide layer was roughly evaluated to be close to 0.1 μm.

Acknowledgement

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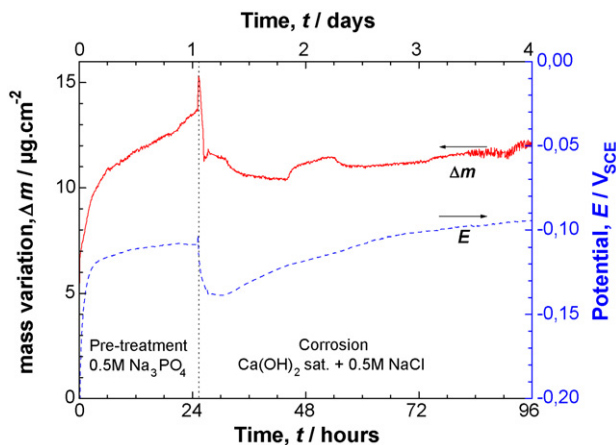
Fig. 5. EQCM data on the mass and potential changes of iron treated during 24 h in a 0.5 M Na₃PO₄ solution then immersed in the corrosion test solution.

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