

Corrosion behaviour of reinforcing steel exposed to an amino alcohol based corrosion inhibitor

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Abstract

Electrochemical impedance measurements were performed in order to obtain information on the corrosion behaviour of reinforcing steel in the presence of a penetrating amino alcohol corrosion inhibitor. The investigation was performed in solutions contaminated with chlorides, in the presence of inhibitor.

The electrochemical results indicate that the inhibitor is able to penetrate through mortar, minimising steel corrosion.
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1. Introduction

The reinforcing steel in concrete is normally protected from corrosion by the formation of a passive film. However, the diffusion of aggressive species, such as chloride ions and carbon dioxide through concrete can breakdown the passive layer, leading to metal dissolution, when they reach the steel–concrete interface. The corrosion process has a strong impact on the durability and performance of reinforced concrete structures and preventive or remedial procedures must be considered. Among the possible solutions to prevent and/or to control reinforcing steel corrosion, the use of penetrating corrosion inhibitors has been a common procedure, since its use is attractive from the point of view of economy and ease of application.

Penetrating corrosion inhibitors (PCIs, also known as MCIs) are compounds able to penetrate through the capillary structure of concrete, first by liquid diffusion via capillary suction and by following hair line and micro cracks present in concrete.

The corrosion behaviour of reinforcing steel in the presence of PCIs has been widely studied [1–6], however the results found in the literature are sometimes contradictory and there is a discussion focussed on the ability of these inhibitors to penetrate into concrete. Recently, the efficiency of these inhibitors has been discussed and there is some criticism regarding their application. Morris and Vazquez [1] concluded that PCIs do not show a substantial improvement of the corrosion resistance of reinforcing steel embedded in concrete samples exposed to chlorides under immersion conditions. Moreover, the same authors found that the performance of these inhibitors depends on the quality of concrete, being better in specimens with higher w/c ratios. Elsener et al. [2,3] found that PCIs do not influence the corrosion rate in mortar specimens exposed to chlorides.

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However, some efficiency can be achieved in simulated pore solution. According to literature [3] one of the inhibitor constituents does not reach the embedded steel, which explains the loss of inhibiting properties. Contrasting to this opinion, other authors claim that PCIs are very effective in reducing reinforcement corrosion [4–6].

The mechanism by which the organic inhibitors provide corrosion protection has also been a point of discussion. Some researchers [7] suggest that they are able to form an adsorption layer on the steel surface, hindering steel dissolution. It has been suggested that mixed-type organic inhibitors influence the kinetics of the anodic and cathodic reactions [8,9]. The use of inhibitors may also affect the chloride threshold value. Some authors report that corrosion inhibitors help to decrease the free chloride content in concrete and/or decrease the rate of diffusion of chloride [10,11].

In previous works electrochemical measurements showed that amino alcohol-based corrosion inhibitors increased the corrosion resistance of steel samples immersed in solutions simulating the concrete pore solution contaminated with chloride [12–14]. Moreover, X-ray photoelectron spectroscopy analysis showed that the inhibitor forms a film containing nitrogen species, which seem to complex the chloride ions [12]. The previous electrochemical measurements also showed that the selected inhibitors are able to reduce the corrosion rate even when steel is under corrosion attack [12,13]. Following these results, the present work aims at studying the ability of an amino alcohol-based inhibitor to penetrate through mortar specimens and at assessing the corrosion behaviour of steel samples immersed in chloride-contaminated solutions.

2. Experimental procedure

2.1. Electrochemical set-up

To study the penetration of the inhibitor into mortar two different electrochemical cells were used. The first consisted of two cylindrical containers separated by a disk of mortar (Fig. 1). Mortar slabs with different thicknesses (1, 2 and 3 cm) were tested. The containers were filled with an extract of pore solution contaminated with 2 g/l NaCl or 4 g/l NaCl. The inhibitor selected was added to the solution in the left side compartment, whereas steel was immersed in the right side solution. Thus, in order to reach the steel the inhibitor must diffuse through the mortar slab.

For the mortar thickness of 1 cm, two concentrations of inhibitor were tested: 2 and 4% vol/vol of inhibitor in the pore solution.

Details on the preparation of the pore solution and steel surface are described elsewhere [12,13].

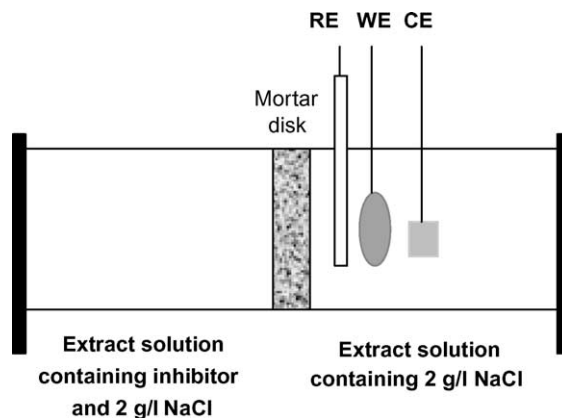


Fig. 1. Electrochemical cell used to study the penetration of the inhibitor through mortar. RE = reference electrode (saturated calomel electrode). WE = working electrode (steel). CE = counter electrode (platinum).

The second electrochemical cell consisted of only one container filled with the cement extract solution (Fig. 2). The mortar disk (1 cm thick) was mounted on the top of this compartment with one face in direct contact with the solution contaminated with 2 g/l NaCl. In this set up, the inhibitor (4% vol/vol) was sprayed on the external side of the mortar disk. The application was performed during two days (3 treatments/per day). The first impedance measurements were performed one day after the last application.

2.2. Mortar composition

The mortar disks were prepared using a mixture of cement, water and sand. The water/cement ratio was 0.6. The amount of sand was three times that of cement. The mortar disks were then cured for 3 days in a high humidity environment (~100% relative humidity) at room temperature.

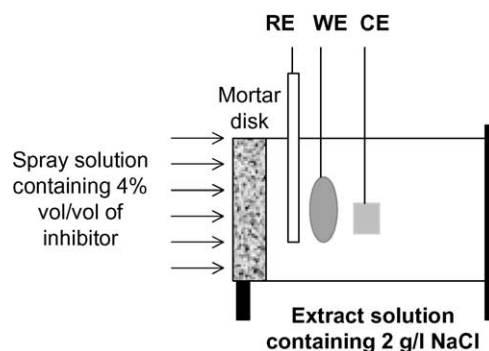


Fig. 2. Electrochemical cell used to study the penetration of the inhibitor through mortar. RE = reference electrode (saturated calomel electrode). WE = working electrode (steel). CE = counter electrode (platinum).

2.3. Techniques

Electrochemical impedance spectroscopy (EIS) measurements were performed using a three-electrode arrangement, consisting of the working electrode (steel) with an exposed area of 3.14 cm^2 , the counter electrode (Pt) and the reference electrode (saturated calomel electrode—SCE). The frequency range was swept between 50 kHz and 0.05 mHz. The amplitude of the wave was 10 mV. All the experiments were conducted at the open circuit potential, which is referred to the reference electrode (SCE). Tests were carried at least on duplicate samples, using distinct steel disks.

3. Results and discussion

3.1. Open circuit potential

Fig. 3 depicts the evolution of open circuit potential of steel samples in solutions with and without inhibitor addition, using the experimental set up shown in Fig. 1. Experiments were performed on the reference system (extract of cement solution + 2 g/l NaCl, without inhibitor addition) and on the system containing 4% (vol/vol) inhibitor. Fig. 3 shows that the potential evolution is different in the presence and in the absence of inhibitor. During the first 2 h both systems showed an increase of the potential towards the anodic values. However, after this period some changes were observed. The potential values for the system without inhibitor decreases with time and stabilises around -300 mV (SCE) after approximately 24 h of immersion. Further, readings shows large fluctuations, revealing corrosion onset. In

the presence of inhibitor the potential also shows some fluctuations during the first 24 h, but thereafter it slowly increases with time, reaching values around -160 mV (SCE). The number and amplitude of the potential fluctuations is much lower than that observed in the absence of inhibitor. In a previous work [12] the potential evolution towards anodic values was attributed to the spontaneous adsorption of an inhibitor film on the iron surface. Thus, the continuous shift of the potential readings towards positive values observed in Fig. 3 suggests that the inhibitor is able to penetrate through the mortar disk, reaching the solution wherein steel is immersed. Here, the inhibitor adsorbs on the steel surface increasing the open circuit potential and hindering the corrosion reactions.

3.2. Electrochemical impedance spectroscopy

3.2.1. Inhibitor dissolved in solution

Fig. 4 depicts the impedance spectra obtained on a sample immersed in the reference system (no inhibitor added) after different immersion times. Initially, there is an increase of the impedance values measured in the low frequency range. After 24 h of immersion the total impedance of the system starts to decrease (Fig. 4), revealing an increase of corrosion activity on the steel surface. The initial increase of the impedance (first 24 h of immersion) results from the formation of a passive film on the steel surface as a consequence of the alkaline nature ($\text{pH} \sim 12.5\text{--}13$) of the working solution. This film is mainly composed of iron oxides and/or hydroxides that are more hydrated in the presence of chloride ions as previously demonstrated [15]. However, with time and due to the presence of chloride ions, the passive

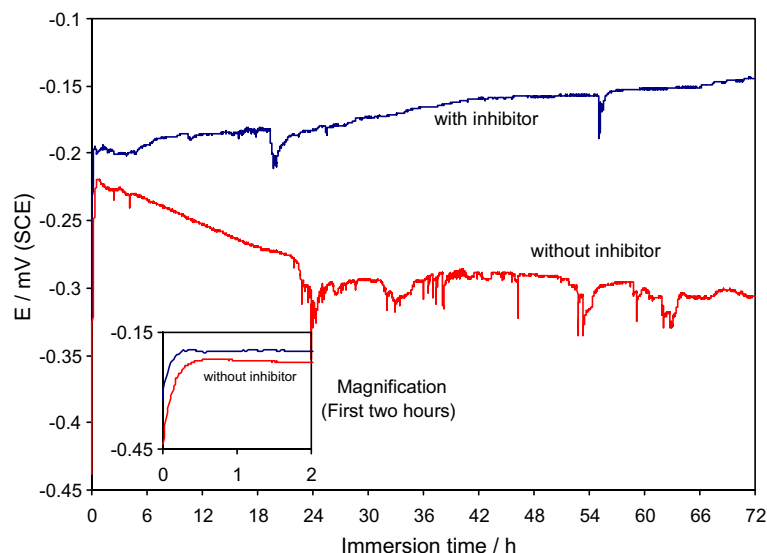


Fig. 3. Open circuit potential for the systems with and without inhibitor, using the electrochemical cell depicted in Fig. 1.

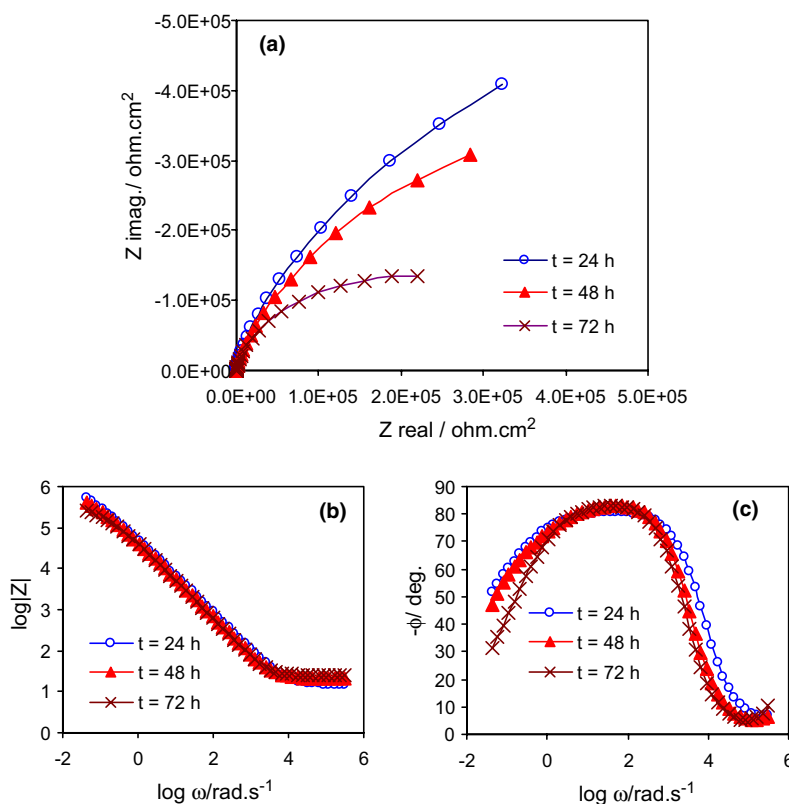


Fig. 4. Impedance spectra obtained for the reference system without inhibitor and with 2 g/l NaCl (see Fig. 1). (a) Nyquist plot; (b) Magnitude Bode plot; (c) Phase angle Bode plot.

film becomes unstable and the corrosion process is initiated, leading to a decrease of the total impedance values and of the phase angle (Fig. 4a,b and c).

Fig. 5 depicts the impedance spectra obtained after different times for a steel sample tested using a mortar disk with 1 cm thickness according to the scheme described in Fig. 1, in the presence of inhibitor. The results show that the total impedance of the system strongly increases with time (Fig. 5a). After 96 h of exposure the total impedance values at low frequency (10^{-1} rad/s) stabilised around $5 \times 10^6 \Omega \text{cm}^2$ (Fig. 5b), revealing an increase of approximately one order of magnitude relative to the initial values. Moreover, the phase angle (Fig. 5c) increases with time, approaching 90° . This trend suggests that the response of the system changes from a resistive behaviour to a capacitive behaviour. This is related with a decrease of the corrosion activity on the surface due to the formation of a protective surface film. These changes clearly demonstrate that the inhibitor diffuses through mortar thereby hindering the corrosion activity on the steel surface.

The decrease of the concentration of inhibitor from 4% to 2% (vol/vol) and the duplication of the chloride content (from 2 g/l to 4 g/l NaCl) did not affect the response of system. In both situations the evolution of the impedance spectra is identical to that observed in Fig. 5. Previous results [12–14] obtained in solutions

simulating concrete also showed that the protective behaviour was not affected when the inhibitor concentration ranged from 1% to 4%. The same trend was observed when the chloride content was duplicated.

The thickness of the mortar through which the inhibitor needs to diffuse was also investigated. Results depicted in Fig. 6 show the impedance spectra obtained for steel samples after one week of immersion using the experimental set-up depicted in Fig. 1. All the systems showed identical behaviour, thus suggesting that after one week the inhibitor reached the solution, independently of the mortar thickness, leading to an increase of the corrosion resistance of the reinforcing steel.

The impedance spectra obtained for the different experimental conditions shows that the electrochemical behaviour of the system changes with time. Thus, initially the system presents a resistive behaviour at low frequencies and, later on, it changes towards a capacitive behaviour. The initial shape of the phase angle plot suggests the presence of two time constants partially superimposed that can be described by the equivalent circuit proposed in Fig. 7. In this equivalent circuit R_s is the electrolyte resistance; R_f the film resistance and R_{ct} the charge transfer resistance. The parameters Q_f and Q_{dl} are associated with the film capacitance and the double layer capacitance, respectively. Their values were obtained by using a constant phase element (CPE), which

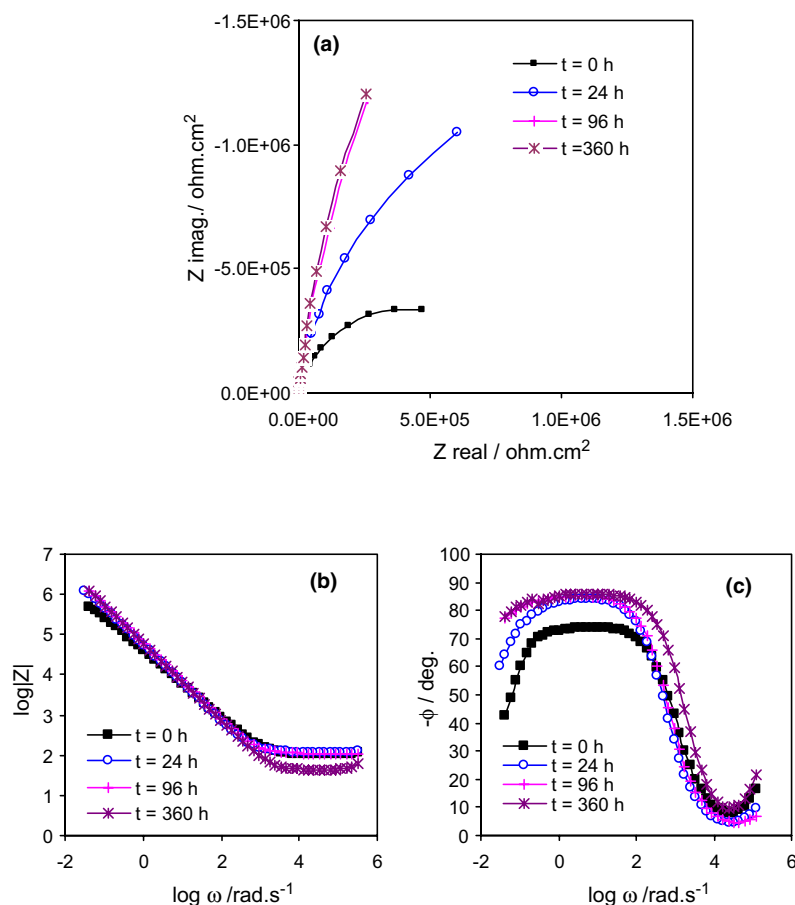


Fig. 5. Impedance spectra obtained for a system with a mortar disk of 1 cm after addition of 4% inhibitor to the extract solution containing 2 g/l NaCl (Fig. 1). (a) Nyquist plot; (b) Magnitude Bode plot; (c) Phase angle Bode plot.

represents a non-ideal frequency dependent capacitance. The CPE behaviour can be the consequence of the fractal nature of the electrode interface or heterogeneity of the steel surface. Associated with the CPE there is a variable value n , which generally ranges between 1 and 0.5 and that describes the distribution of the dielectric relaxation times in the frequency domain. When n is close to 1, the CPE represents a capacitor.

For the electrochemical cell described in Fig. 1, using mortar disks with different thickness, the evolution of the film resistance (R_f) and film capacitance (Q_f) are depicted in Figs. 8 and 9, respectively. The evolution of the film resistance can be considered as an indicator of the protective behaviour of the inhibitor film formed on the surface. Fig. 8 shows that the film resistance strongly increases with time. Initially the resistance values are in the range 6×10^4 – $3 \times 10^5 \text{ ohm cm}^2$ but with time the resistance increases and the largest values were found for the thicker mortar disks ($\sim 6 \times 10^6 \text{ ohm cm}^2$).

The evolution of the film capacitance, as shown in Fig. 9 is characterised by a slow decrease toward values in the range of 20–30 $\mu\text{F/cm}^2$. This decrease may indicate thickening of the protective film and/or an increase of its homogeneity. Since the changes in the capacitance are

very small, whereas that of resistance are much larger, it can be suggested that the film homogeneity controls the corrosion behaviour of the system, rather than film thickness.

3.2.2. Inhibitor applied by spraying

The inhibitor was applied on the surface of a mortar disc with a thickness of 1 cm (according the scheme depicted in Fig. 2). Fig. 10 shows the impedance spectra obtained after different periods of immersion. The first impedance spectra was obtained at the end of the spraying procedure, corresponding to $t = 0 \text{ h}$ in Fig. 10. The results show that the low frequency impedance of the system increased with time, attaining values above $1 \times 10^6 \text{ ohm cm}^2$ (Fig. 10b). The evolution of the phase angle (Fig. 10c) after 168 h (one week) in the low frequency region shows an increase of the phase angle, revealing that the response of the system is very close to that of a capacitor. The evolution of the film resistance and capacitance was compared with the values obtained when the inhibitor was added to the solution (using the cell depicted in Fig. 1) and the results are depicted in Figs. 11 and 12, respectively. When the inhibitor is applied by spray on the mortar surface the increase of the

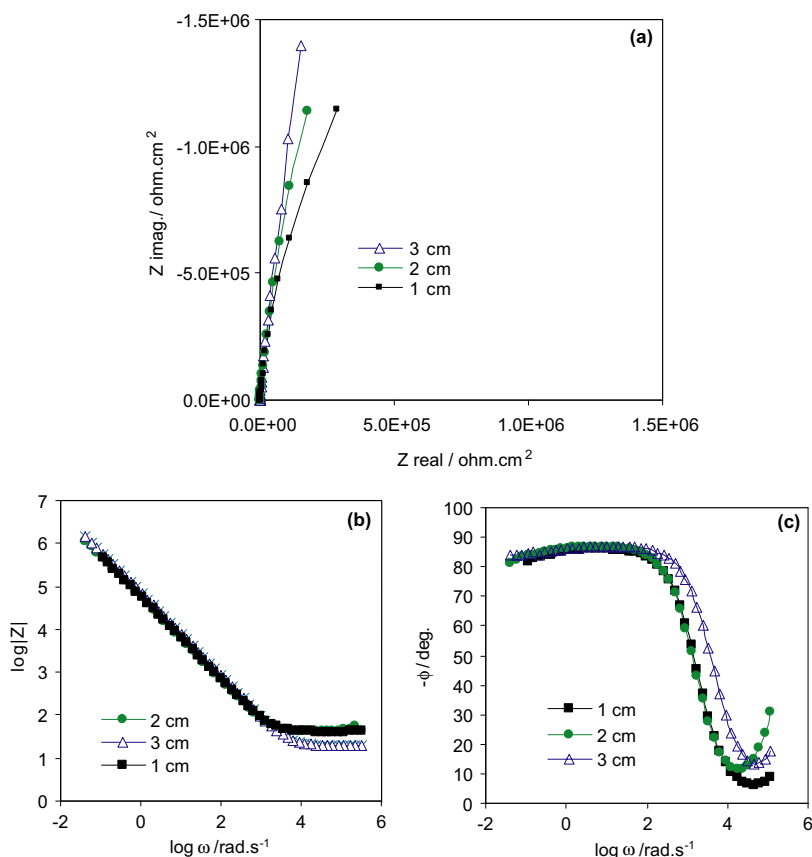


Fig. 6. Impedance spectra obtained for systems with mortar disks of 1, 2, and 3 cm after 7 days of exposure to the solution containing 4% inhibitor and 2g/l NaCl (Fig. 1). (a) Nyquist plot; (b) Magnitude bode plot; (c) Phase angle bode plot.

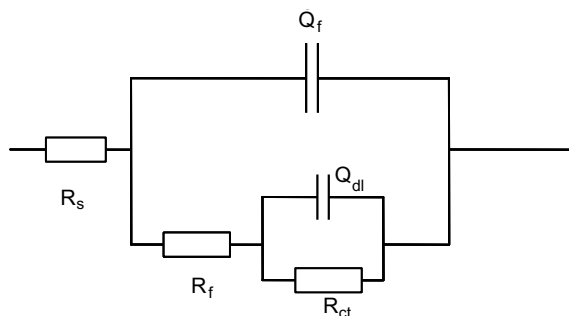


Fig. 7. Equivalent circuit used for the numerical fitting of the impedance spectra.

film resistance is more gradual, stabilizing after approximately 100 h. When the inhibitor was dissolved in solution, the stabilization of the resistance values occurred after approximately 48 h. Although a longer time is required to obtain the same degree of protection the inhibitor applied by spraying diffuses through the mortar, reaching the steel. The capacitance values (Fig. 12) are not sensitive to the method of inhibitor application.

The evolution of the charge transfer resistance, which is an indicator of the corrosion rate, was also determined for the different systems as shown in Fig. 13.

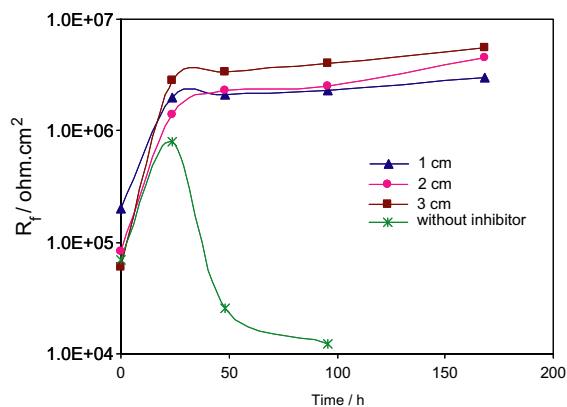


Fig. 8. Film resistance for steel samples tested using the scheme depicted in Fig. 1, using mortar disks with different thickness.

In the absence of inhibitor the charge transfer resistance increased during the first day of immersion, but later on it started to decrease as expected due to passive film breakdown induced by the chloride ions. After 48 h of immersion the charge transfer resistance is around 20 000 ohm cm², corresponding to a corrosion rate above 1 μA/cm², which can be considered critical, according to Andrade et al. [16]. However, in the presence of

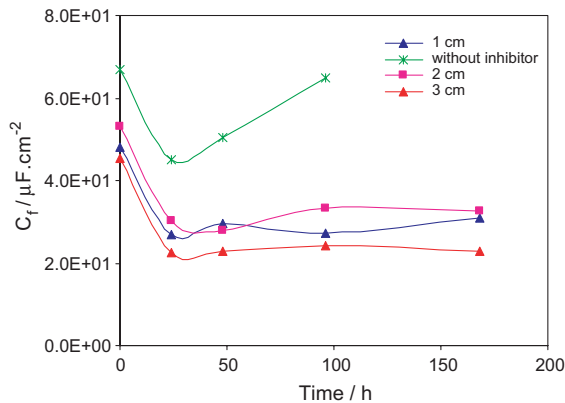


Fig. 9. Film capacitance for steel samples tested using the scheme depicted in Fig. 1, using mortar disks with different thickness.

inhibitor, the charge transfer resistance increased gradually (Fig. 13) and consequently the corrosion rate decreases by more than one order of magnitude, attaining values around $0.1 \mu\text{A}/\text{cm}^2$. The method of inhibitor application affects the early stages of the corrosion process. When the inhibitor is applied by spray the initial values of the charge transfer resistance (Fig. 13) are identical to those calculated in the absence of inhibitor. However, after 72 h of exposure the charge transfer resistance starts to increase, revealing a decrease in the

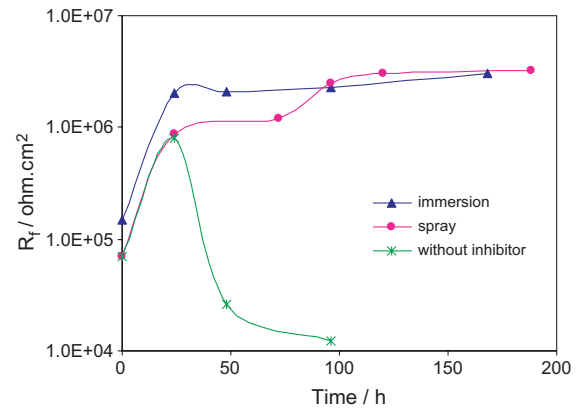


Fig. 11. Film resistance for mortar samples with 1 cm thickness and different application procedures.

corrosion rate. In the presence of inhibitor, for both application procedures, the charge transfer resistance stabilizes around $2 \times 10^5 \text{ ohm}/\text{cm}^2$. Furthermore, for these samples the film resistance is above $2 \times 10^6 \text{ ohm}/\text{cm}^2$, suggesting the presence of a protective homogeneous layer on the steel surface.

The electrochemical impedance results show that the effect of the inhibitor addition on the corrosion rate of reinforcing steel is dependent on the method of application. Thus, when the inhibitor is sprayed on mortar the

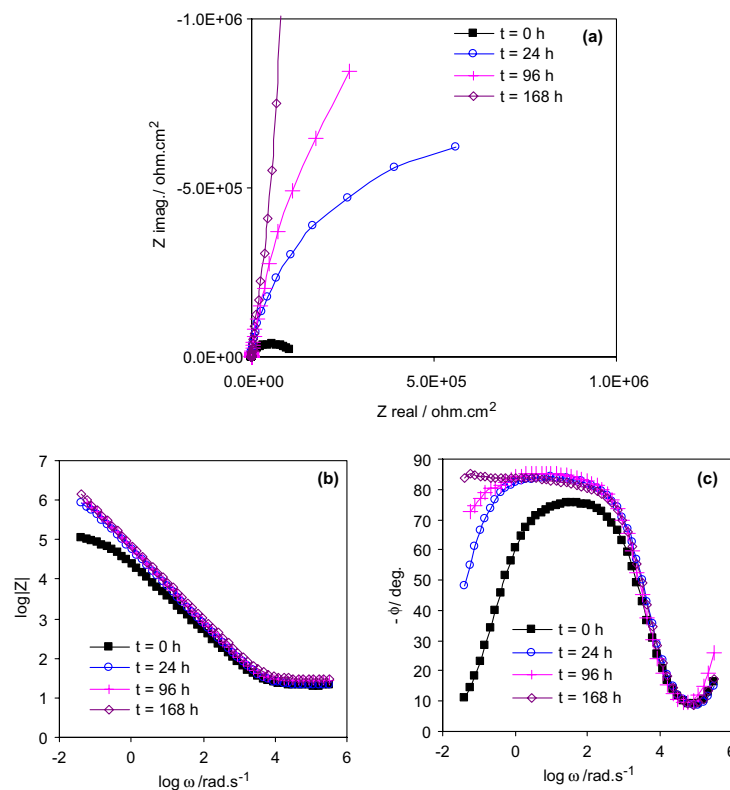


Fig. 10. Impedance spectra obtained for a system with a mortar disk of 1 cm after spraying a solution containing 4% (vol/vol) of inhibitor on the mortar surface (Fig. 2). (a) Nyquist plot; (b) Magnitude Bode plot; (c) Phase angle Bode plot.

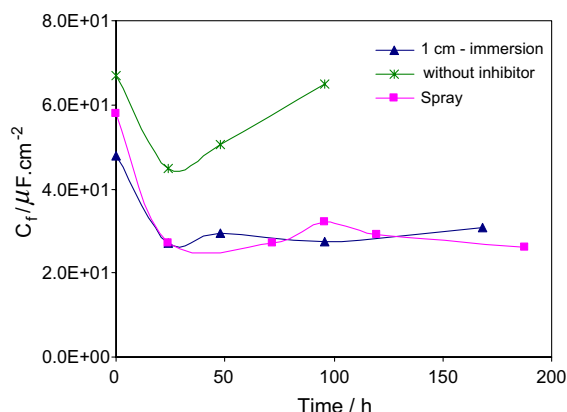


Fig. 12. Film capacitance for steel samples. Different application procedure using mortar specimens with 1 cm.

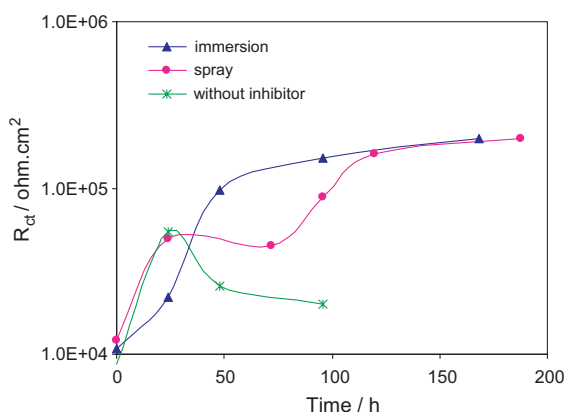


Fig. 13. Charge transfer resistance for steel samples. Different application procedure using mortar specimens with 1 cm.

corrosion inhibition is delayed comparatively to the situation in which the inhibitor is dissolved. However, later on identical corrosion rates were measured.

The results obtained in the present work illustrate the corrosion protection provided by a penetrating corrosion inhibitor on steel samples exposed to an environment simulating that found in concrete. The inhibitor was tested in two different conditions and, in both cases, the inhibitor leads to increased corrosion protection.

4. Conclusions

The amino alcohol based corrosion inhibitor tested in this work decreases the corrosion rate of the reinforcing steel. The charge transfer resistance as well as the film

resistance show an important increase in the presence of the inhibitor.

The inhibitor penetrates into the mortar, leading to the formation of a protective film on the steel surface. The resistance of this protective film increases with time, being independent of the mortar thickness, through which the inhibitor needs to penetrate. However, the beneficial effects seem to be delayed when the inhibitor is sprayed on the mortar surface. The procedure used for the application of inhibitor does not affect the corrosion inhibiting performance.

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