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A migrating corrosion inhibitor evaluated in concrete containing various contents of admixed chlorides

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Abstract

The performance of a surface-applied migrating corrosion inhibitor (MCI) based on an alkylaminoalcohol was evaluated on concrete specimens containing reinforcing steel bar (rebar) segments. Two water/cement ratios (w/c's), various chloride contents and two exposure conditions were investigated. The inhibiting efficiency was followed over a period of 1000 days by means of parameters such as corrosion potential, corrosion current and electrical resistance. Results show that when concrete is exposed to the marine environment, the inhibitor is able to reduce the corrosion rate (CR) only when the initial chloride content is below 0.16 wt.% relative to cement content. Efficiency increases as the w/c increases. There is no beneficial effect when the initial chloride content is greater than 0.43%. When concrete is immersed in a saline solution, no beneficial effect associated to the use of the inhibitor could be appreciated, regardless of w/c or initial chloride content in concrete. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Corrosion of reinforcing steel bars (rebars) in concrete is a serious and significant problem from both the economics and structural integrity standpoints. Many are the approaches that can be used to mitigate corrosion of reinforcing steel, among which, protective coatings and sealers, cathodic protection, concrete realkalinization and corrosion inhibitors are commonly employed. The use of corrosion inhibitors is probably more attractive from the point of view of economics and ease of application [1]. The application of corrosion inhibitors in reinforced concrete is possible by adding it to the mixing water during the concrete preparation or by applying it to the external surface of hardened concrete. In this last case, the inhibiting compound should diffuse through the concrete cover and reach the rebar in a sufficiently high concentration to protect steel against corrosion. Reviews of the most commonly used corrosion inhibitor types in concrete repair systems [2] and the various possible mechanisms of inhibition have been recently published [3].

Over the last years, the use of organic inhibitors, as an alternative to the more commonly employed calcium nitrite-based inhibitors, has been increasing. Organic inhibitors offer protection by adsorbing and forming a protective film on the steel surface. Usually, there is a polar group in the organic molecule that adsorbs on the metal and a nonpolar hydrophobic chain oriented perpendicular to this surface. These chains act, on the one hand, by repelling aggressive contaminants dissolved in the pore solution, and on the other, by forming a tight film (barrier) on the metallic surface. Duprat and Dabosi [4] examine the effect of various aminoalcohols as corrosion inhibitors of carbon steel in 3% NaCl solutions. The efficiency of the inhibitor increases when only one of the hydrogen atoms of the amino group is substituted, as the remaining one induces hydrogen bonds formation between surface-chelated molecules. In the case of 2-ethylamino-ethanol [5], the inhibitive action in 3% NaCl solutions was interpreted both by its stabilisation effect on the prepassive ferrous hydroxide films and by its adsorp-

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tion through surface chelate formation onto bare metal sites. The effect of pH on the inhibitive efficiency was also investigated.

Contradictory results have been recently reported when testing corrosion inhibitors in simulated pore solutions and in mortars [6–8]. Elsener et al. [6] studied the efficiency of an inhibitor based on alkylamines on steel corrosion in mortars and in calcium hidroxide solutions. In mortars, there is no apparent inhibition of pitting or a decrease in corrosion rate (CR), but the initiation of the corrosion process appears to be delayed. The beneficial effect decreases on carbonated mortars. In a recent publication of these same authors [7], the discrepancy between the observed high diffusion rate of the migrating corrosion inhibitor (MCI) in mortar and the lack of corrosion inhibition was rationalised by the fact that only the diffusion of the volatile phase was measured. Migration of the nonvolatile component (carbonic acids) through concrete was not proved and assumed to be slow. Thus, the inefficiency detected in concrete, as compared to solutions, should be related to the inability of the nonvolatile components to reach the steel bars. In turn, Mammoliti et al. [8] assumed that the difference in the inhibitors efficiency tested in concrete or in synthetic pore solutions is the result of the dependence of the inhibition mechanism on chemical reactions within the cement phase. The present study aims at evaluating the performance of a surface-applied migrating corrosion inhibitor based on an alkyl-aminoalcohol on concrete specimens containing rebar segments. Two water/cement ratios (w/c's), and two exposure conditions were investigated.

2. Experimental

2.1. Concrete specimens preparation

Samples prepared for electrochemical testing consisted of cylindrical concrete specimens containing four rebar segments, as can be seen in Fig. 1. Rebars have a diameter of 1 cm and present an exposed area of 40 cm^2. They are placed in such a way that a concrete cover of 1.5 cm is achieved. As part of an ongoing investigation on rebar coatings, two of the four rebar segments of each specimen were coated with epoxy paint. The performance of this and other type of coatings was analysed in a previous publication [9].

In addition, standard size concrete specimens 15 cm in diameter and 30 cm tall were prepared following the ASTM C-39 standard in order to determine the compressive strength of the different concrete mixes selected for the study. Two types of concrete, a *standard quality* ($\sigma'_{BM} \approx 20$ MPa) prepared with a w/c of 0.60 and a cement content of 300 kg/m^3, and a *good quality* ($\sigma'_{BM} \approx 30$ MPa) concrete prepared with w/c = 0.40 and a cement content of 400 kg/m^3 were tested. The influence of admixed chlorides on the inhibitor efficiency was evaluated by testing three different chloride contents on the concrete mix. This aspect was of great interest as in many coastal cities of Argentina this type of inhibitor is frequently recommended to prevent rebar corrosion in concrete structures build using sea sand as a fine aggregate. A mix with no admixed chlorides was also prepared to be used as reference.

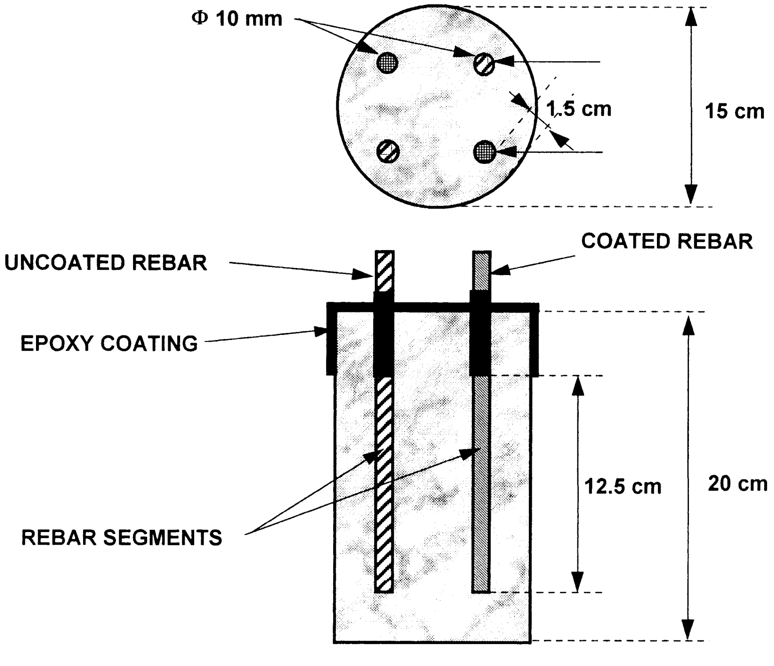

Fig. 1. Schematic representation of the cylindrical concrete test sample used in the study.

Table 1
Mix design composition

Mix design identification	A	B	C	D
Cement content (kg/m^3)	300	400	300	300
Water (l)	180	160	180	180
Fine aggregate (FA)				
River sand (kg)	–	–	851	858
Sea sand (kg)	858	789	–	–
River rock MAS = 10 mm (kg)	1003	1042	1003	1003
Sodium chloride (kg)	–	–	7.4	–
Superplastisizer	1.0	2.5	–	–
Water/cement ratio (w/c)	0.60	0.40	0.60	0.60
Fine aggregate/total aggregate	0.46	0.43	0.46	0.46
% $\mathrm{Cl_o}^-$	0.78	0.43	1.60	0.16
Slump test (cm)	3.0	3.0	6.5	8.0

Table 1 presents in greater detail the composition of the four different mix designs that were selected for this study. The total chloride concentration in the concrete mixes was determined following the ASTM C1152 standard. Mixes A and B were prepared using sea sand of the same type used by the local construction industry (siliceous, fines modulus = 2.7 ± 0.3 and specific gravity = 2.7). The other two mixes (C and D) were prepared using river sand (fines modulus = 2.7 and specific gravity = 2.65) containing less than 0.1% per weight of chloride ions.

The inhibitor investigated is designed to be applied on the external surface of hardened concrete. This commercial formulation relies on migration of the active component to reach the rebar surface. The inhibitor blend is based on alkylaminoalcohols and will be referred to as "inhibitor" from here on. A model for the interaction between steel surfaces and formulations based on a similar compound has been proposed by Welle et al. [10] on the basis of XPS measurements.

Chemical tests were undertaken in order to evaluate the presence of the corrosion inhibitor at the rebar surface in a sufficient concentration. Analyses were based on a colorimetric method proposed by the manufacturer of the inhibitor.

2.2. Identification and conditioning of specimens

A total of 32 specimens (eight specimens per each mix design) were prepared. The inhibitor was applied on four specimens per each mix design. The other four specimens were left as blanks with no inhibitor application.

The specimens containing rebars were demolded 24 h after casting and were kept in a laboratory environment (20 °C, 65% RH) for the following 6 days. The inhibitor was applied only on the cylindrical surface of the specimens 7 days after demolding, following the recommendations given by the manufacturer. The average amount of product applied to the specimens is 480 ± 10 g/m^2.

Table 2 presents the specimens identification, indicating in each case the exposure condition, mix design and whether or not the corrosion inhibitor was applied. Duplicate specimens were prepared.

Before exposing the specimens to the selected environments, they were kept for 60 days in an indoors environment. During this period, several nondestructive electrochemical measurements were performed periodically.

2.3. Exposure conditions

Two exposure conditions were selected for the study. They will be referred to as "marine" and "immersion", respectively.

Two blank specimens (with no inhibitor) and two treated with the inhibitor were exposed to a so-called "marine" environment. These specimens were placed in a metallic cage located at the top terrace of a forty-floor building in Mar del Plata (3756° S latitude, 5735° W longitude). This terrace is 120 m above sea level and is located at approximately 100 m from the seashore. Samples are directly exposed to rainfall, sea spray and wind. The environmental conditions at this coastal city are characterised by high humidity, temperatures ranging from 14 to 27 °C during the summer and from 3 to 13 °C during winter and an average monthly rainfall of 90 mm. In addition, two specimens of each mix design, with and without inhibitor, were partially immersed in an aerated solution containing 3.5% Cl^-.

2.4. Electrochemical measurements

The corrosion progress was monitored in time following the variations of the main electrochemical parameters: the corrosion potential E_{corr}, the electrical resistance R_{s} and the polarization resistance, R_{p}. The last parameter was used to estimate the rebar corrosion rate, CR.

The corrosion potential was measured using a high impedance voltmeter (HP E2378A) against a standard Cu/$\mathrm{CuSO_4}$ saturated reference electrode (CSE).

Table 2
Specimen identification and characteristics

			Mix design	
Specimen identification	Exposure condition	Inhibitor application	w/c	Fine aggregate
A 1 and 2	Immersion	No	0.6	Sea sand
A 3 and 4	Marine	No	0.6	Sea sand
AI 1 and 2	Immersion	Yes	0.6	Sea sand
AI 3 and 4	Marine	Yes	0.6	Sea sand
B 1 and 2	Immersion	No	0.4	Sea sand
B 3 and 4	Marine	No	0.4	Sea sand
BI 1 and 2	Immersion	Yes	0.4	Sea sand
BI 3 and 4	Marine	Yes	0.4	Sea sand
C 1 and 2	Immersion	No	0.6	River sand
C 3 and 4	Marine	No	0.6	River sand
CI 1 and 2	Immersion	Yes	0.6	River sand
CI 3 and 4	Marine	Yes	0.6	River sand
D 1 and 2	Immersion	No	0.6	River sand
D 3 and 4	Marine	No	0.6	River sand
DI 1 and 2	Immersion	Yes	0.6	River sand
DI 3 and 4	Marine	Yes	0.6	River sand

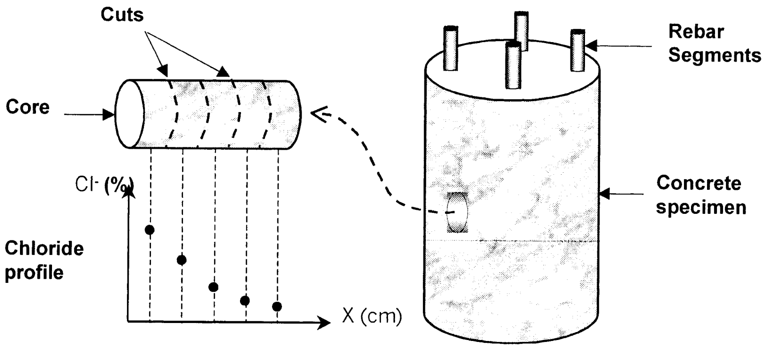

Fig. 2. Schematic representation of the coring and chloride profile determination procedure.

The electrical resistance (R_s) was measured between the two uncoated rebar segments using a Nilsson 400 soil resistivity meter. This instrument uses a square wave of 97 Hz, preventing polarization of the electrodes. The electrical resistivity of concrete (ρ) was calculated as $\rho = kR_s$, where $k = 7.5$ and 12 cm for the marine and immersed condition, respectively [11].

Polarization resistance (R_p) was evaluated as $\Delta V/\Delta i$, from potential sweeps up to ± 0.01 V from E_{corr} at a scan rate of 10^{-4} V s^{-1}. Experiments were performed using a CMS100 from Gamry Instruments potentiostat. The results were corrected to compensate the IR drop error. CR, in terms of corrosion current density, can be evaluated through polarization resistance according to the Stearn–Geary relationship [12] as (Eq. (1)):

$$i_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{R_p} \tag{1}$$

where β_a and β_c are the anodic and cathodic Tafel slopes, respectively, which are kinetic parameters characteristic of each metal–solution system. Due to its dependence on the Tafel slopes, B values should take into account whether the metal is in the active or passive state. Based on polarization resistance and gravimetric measurements, Gonzalez et al. [13] reported typical values of B for steel embedded in mortar. According to them, the value of B for bare steel in the passive state (typically $E_{corr} > -0.2$ V vs. CSE [14]) is 0.052 V. On the other hand, for bare steel in the active state (typically $E_{corr} < -0.35$ V vs. CSE [14]), the corresponding values of B is 0.026 V.

Assuming uniform corrosion on the entire bar surface, the nominal value of CR in μm year^{-1} can be calculated using Faraday's law as:

$$\mathrm{CR} = \frac{K a_w}{nF\delta} i_{corr} = \alpha i_{corr} \tag{2}$$

where $K = 315\,360$ is a unit conversion factor, F is the Faraday constant ($F = 96485$ C mol^{-1}), n is the number of moles of electrons transferred, a_w is the atomic weight of iron in grams, δ is the density of the metal in g cm^{-3} and i_{corr} is the current density in μA cm^{-2}. Therefore, the value of the constant α for steel is approximately $\alpha_{Fe} = 11.6$ μA^{-1} cm^2 μm year^{-1} in each case.

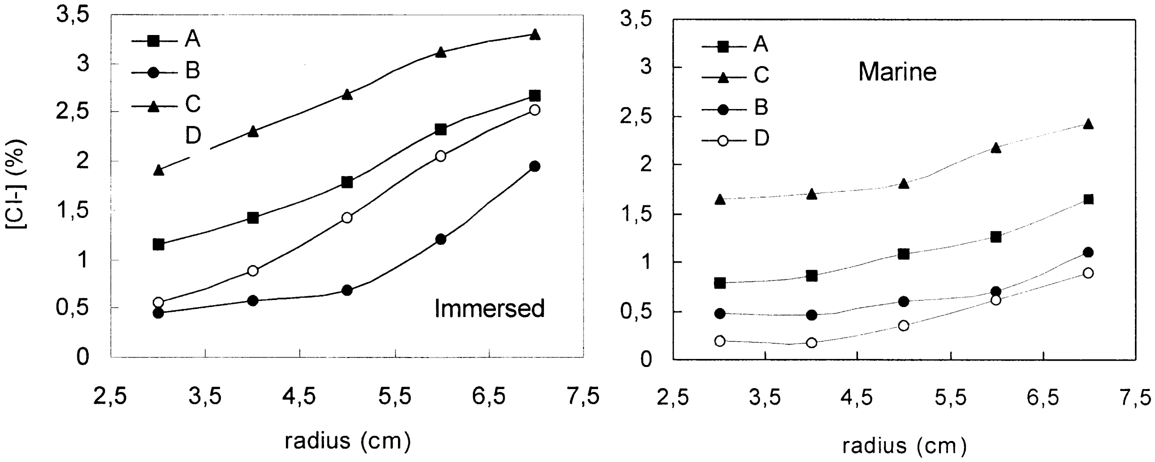

Fig. 3. Chloride concentration profiles obtained from concrete specimens after 900 days of exposure to the immersed condition (left) and seashore environment (right). The diameter of the specimens is 15 cm and r is the radius.

Table 3
Chloride effective coefficient (D_{eff}) and surface concentration (C_s) obtained from the mathematical curve fitting of the experimental data shown in Fig. 3

	Immersed condition		Marine environment	
Concrete mix	D_{eff} (cm^2 s^{-1})	C_s (%)	D_{eff} (cm^2 s^{-1})	C_s (%)
A	5.09×10^{-8}	3.2	4.83×10^{-8}	1.9
B	1.88×10^{-8}	2.4	1.79×10^{-8}	1.5
C	5.95×10^{-8}	3.8	4.53×10^{-8}	2.8
D	4.84×10^{-8}	3.2	3.88×10^{-8}	1.2

2.5. Chemical analysis

Chloride concentration profiles were obtained from concrete cores extracted from the test specimens after approximately 900 days of exposure to both marine and immersed condition. Cores were cylindrical, 2 cm in diameter and approximately 5 cm long. Fig. 2 illustrates the core extraction method and the chloride profile determination procedure. In order to analyse the chloride transport mechanism within the concrete specimens, the effective diffusion coefficient (D_{eff}) was determined by solving Fick's second law expressed in cylindrical coordinates as,

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD_{\mathrm{eff}}\frac{\partial C}{\partial r}\right) \qquad (3)$$

where C is the total chloride concentration, r is the radius and t is the time. When solving Eq. (3), the chloride surface concentration (C_s) was assumed to remain constant in time for the immersed specimens. In the case of the marine specimens, C_s was assumed to vary linearly in time, from the initial concentration (C_o) at time $t=0$, to $C=C_s$ at $t=900$ days.

3. Results and discussion

3.1. Characteristics of the concrete mixes

The values of $\mathrm{Cl_o}^-$ shown in Table 1 represent the initial total chloride concentration expressed as percentage by weight of chlorides with respect to the cement content in each concrete mix. Fig. 3 presents the chloride concentration profiles obtained from the concrete cores extracted from specimens exposed to the marine and immersed conditions. Table 3 presents the chloride effective diffusion coefficient (D_{eff}) obtained by fitting the solution of Fick's second law to the experimental data shown in Fig. 3. As could be expected, the highest D_{eff} values correspond to concrete mixes prepared with w/c = 0.6 and the lowest value to mix B prepared with w/c = 0.4. The boundary conditions used for solving the solution of Eq. (3) were discussed elsewhere [15]. Fig. 4 shows the evolution in time of the calculated chloride concentration at the rebar surface. These curves are obtained replacing the values of D_{eff}, C_s and C_o calculated for each mix.

Table 4 presents the compressive strength (ASTM C-617) for each of the four concrete mixes tested.

3.2. Corrosion potential (E_{corr})

Fig. 5a and b presents the variation of the rebar corrosion potential in time for the specimens (blank and treated with inhibitor) exposed to the marine environment. The mean E_{corr} values for two duplicate specimens were calculated. Scatter in the potential trends can be attributed to seasonal variations of temperature, relative humidity and rainfall.

The blank and the treated specimens showed no significant difference between the rebar corrosion potential trends obtained on each of the three mixes containing admixed chlorides (A, B and C). The difference in the rebar corrosion

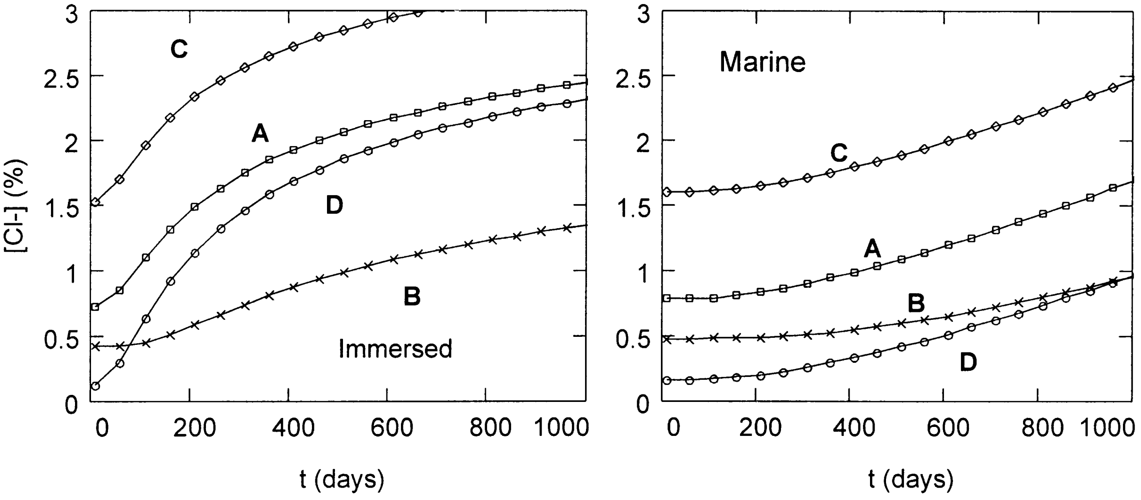

Fig. 4. Variation of the chloride concentration (relative to concrete weight) in time at the rebar surface (concrete cover = 1.5 cm) for the specimens exposed to seashore (left) and immersed (right) condition.

Table 4
Compressive strength at 7 and 28 days

Concrete mix	Compressive strength (MPa)	
	7 days	28 days
A (FA = sea sand, w/c = 0.60)	14.4	21.3
B (FA = sea sand, w/c = 0.40)	21.5	31.4
C (FA = river sand, w/Cl^-, a/c = 0.60)	16.2	21.0
S (FA = river sand, w/c = 0.60)	14.0	22.5

potential trend of mix D (w/c = 0.6 and no admixed chlorides) became evident after approximately 400 days of exposure. After this period, the E_{corr} values of the blank specimens start shifting towards more negative potentials. This behaviour could be caused by the increase of chloride concentration at the rebar surface coming from the environment (see Fig. 4). On the other hand, the rebar corrosion potential values of the treated specimens show an increasing trend in time, reaching values characteristic of passive steel. Therefore, even when blank and treated specimens present similar chloride concentrations at the rebar surface, the presence of the inhibitor in mix DI seems to maintain the passive state of steel.

As could be expected, specimen C (w/c = 0.6, $\mathrm{Cl_o}^- = 1.65\%$) presents the most negative potential values of the group. These values are typical of steel undergoing active corrosion ($E_{\mathrm{corr}} < -0.35$ V vs. CSE) [14].

The E_{corr} values measured on both blank and treated specimens exposed to the immersed condition, were typical of steel in the active state of corrosion ($E_{\mathrm{corr}} < -0.35$ V vs. CSE). Average results for the immersed condition are summarised in Table 5. Specimens B, prepared with w/c = 0.4, present average E_{corr} values of -0.5 V, which were about 0.1 V more positive (less active) than the values recorded in specimens A, C and D. As in the previous condition, but now for all the mixes under study, the rebar corrosion potential trends show no significant difference between blank and treated specimens. Furthermore, no appreciable difference is observed between the E_{corr} values measured in the three concrete mixes prepared with w/c = 0.6, regardless of their chloride content.

As expected, the corrosion potential values measured on the marine specimens present in general, less active values than the corresponding ones recorded in the immersed condition. This last one certainly represents the most aggressive environment.

3.3. Electrical resistance (R_s)

Fig. 6a and b present the variation of the electrical resistance (R_s) on the blank and the treated with inhibitor specimens, respectively, exposed to the marine environment. Both figures show that mix B, prepared with w/c = 0.4, achieves the highest R_s values, and therefore higher concrete resistivity (ρ) values, of the group. After approximately 1000 days of exposure, the values of R_s were 4.8 and 7.1 kΩ for the treated and blank specimens, respectively. The blank specimens prepared with w/c = 0.6 (A, C and D) presented comparable trends, achieving values of R_s that varied between 1.8 and 3.6 kΩ. Consequently, mix B (good quality concrete, w/c = 0.4) presented the highest resistivity values (approximately 53 kΩ cm for the blank specimens) of the group and mixes A, C and D (standard quality concrete, w/c = 0.6) presented values of ρ varying between 13 and 24 kΩ cm. An evaluation of the degree of corrosion of reinforcing steel by means of concrete resistivity measurements on a similar system has been presented elsewhere [15].

A correspondence between R_s values and chloride content in each mix was observed only on the treated specimens AI, CI and DI (w/c = 0.6). Values of R_s increased from 1.6 to 3.6 kΩ as the chloride concentration in these mixes decreases.

After approximately 1000 days of exposure to the marine condition, the treated specimens prepared with mix D (w/c = 0.6, no admixed chlorides) present R_s values that are almost two times greater than the corresponding values measured on the blank specimens. This behaviour could be attributed either to an increase in the resistivity of concrete due to the application of the inhibitor, or to the formation of

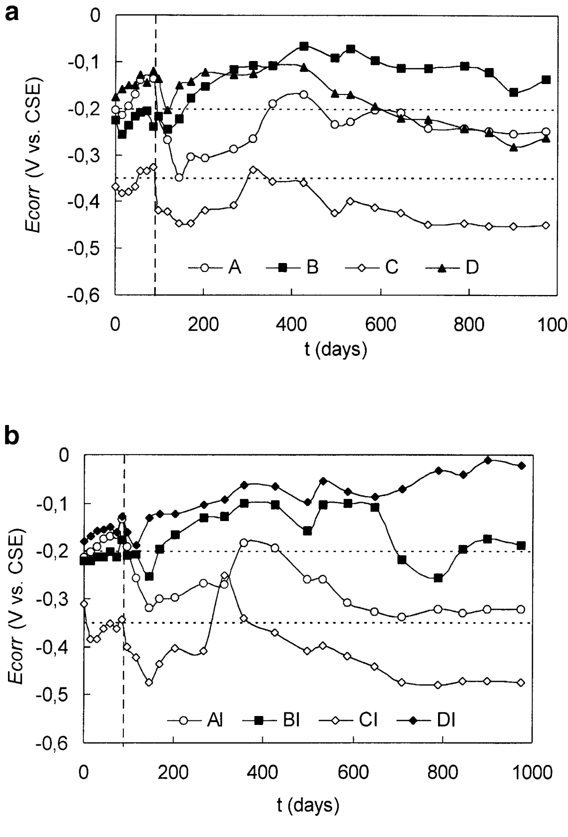

Fig. 5. Variation of the rebar corrosion potential (E_{corr}) with time for the four mix designs under study. Mean values for duplicate specimens are presented. Samples were exposed to the marine environment. (a) Blank specimens. (b) Treated with inhibitor.

Table 5
Average values of corrosion potential, corrosion rate and resistivity measured for each of the four mix designs and the two exposure conditions over the last year of the study

Specimens		E_{corr} (V vs. CSE; average of the last 44 values)		CR (μm year^{-1}; average of the last 12 values)		ρ (Ω cm; average of the last 36 values)	
		Marine	Immersed	Marine	Immersed	Marine	Immersed
Blank	A	− 0.24	− 0.65 ± 0.026	2.2	15.9 ± 4.9	18031	4935 ± 650
	B	− 0.13	− 0.51 ± 0.032	0.5	6.4 ± 1.2	41563	9385 ± 1250
	C	− 0.45	− 0.62 ± 0.015	22.0	51.8 ± 6.6	11531	4053 ± 550
	D	− 0.25	− 0.60 ± 0.020	1.1	8.5 ± 1.4	12813	3948 ± 600
Treated with inhibitor	A	− 0.33	− 0.64 ± 0.030	3.4	15.2 ± 5.1	18281	4965 ± 650
	B	− 0.19	− 0.48 ± 0.045	0.8	10.2 ± 5.0	35727	16400 ± 900
	C	− 0.47	− 0.58 ± 0.022	41.5	40.1 ± 11.6	10344	4070 ± 300
	D	− 0.04	− 0.62 ± 0.018	0.2	3.4 ± 0.7	21133	3835 ± 550

a protective layer on the rebar surface. Preliminary investigations based on electrochemical impedance spectroscopy measurements tend to indicate that both the increase in the electrical resistivity of concrete and the presence of a protective layer on the rebar surface are responsible for the good performance of the inhibitor, when applied on concrete with no admixed chlorides.

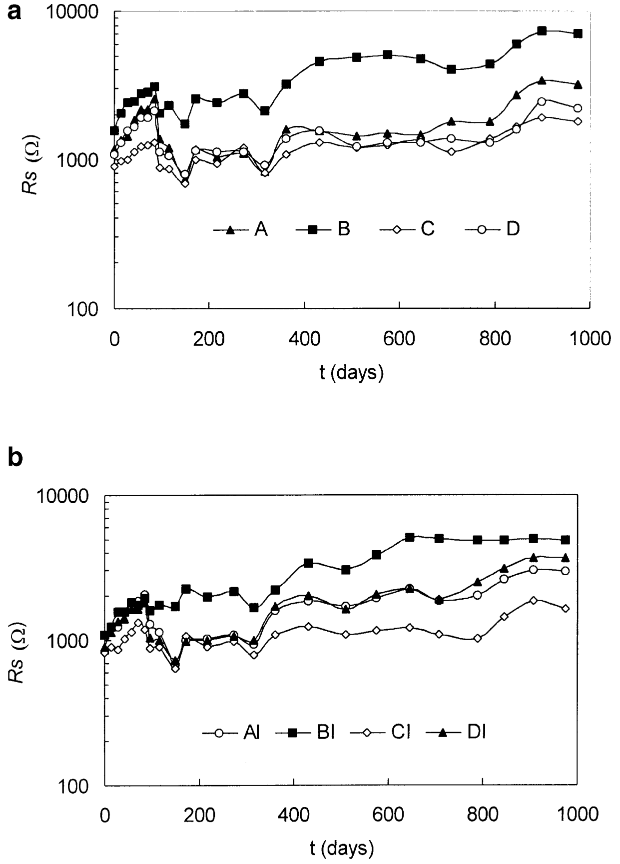

Fig. 6. Variation of the electrical resistivity of concrete (ρ) as a function of time for the four mix designs under study. Mean values for duplicate specimens are presented. Samples were exposed to the marine environment. (a) Blank specimens. (b) Treated with inhibitor.

The average electrical resistance values measured over the last year of exposure to the immersed condition are summarised in Table 5 for each mix. As in the previous condition, a clear difference is observed between the electrical resistance and concrete resistivity values measured on the immersed specimen B (w/c = 0.4), compared to specimens A, C and D (w/c = 0.6), regardless of chloride content in the concrete and the presence of the inhibitor. After approximately 1000 days of immersion, the higher quality concrete (mix B) presented average values of $R_s \approx 1.3$ kΩ ($\rho \approx 10$ kΩ cm). On the other hand, the lower quality concretes, represented by mixes A, C and D, showed R_s values of approximately 0.5 kΩ ($\rho \approx 4$ kΩ cm).

3.4. Corrosion rate

Fig. 7a and b present the rebar CR evolution in time for the blank and treated specimens exposed to marine environment. CR values where calculated from polarization resistance measurements (see Eq. (2)). No significant difference was observed between the CR values measured on blank and treated specimens prepared with admixed chlorides (A, B and C). As could be expected, the rebar CR of both blank and treated specimens increased as the initial chloride content in these mixes increased. In the case of mix D (no admixed chlorides, w/c = 0.6), the treated specimens presented CR values that were almost one order of magnitude lower than the values measured on the blank specimens. Even accepting some dispersion in the measured CR values, the decrease is significant. Only in the case of the specimen D treated with the inhibitor do the CR measurements fall clearly below 1 μm year^{-1}, corresponding to rebars in the passive state.

The average CR values measured over the last year of exposure to the immersed condition are summarised in Table 5 for each mix. As expected, the CR values obtained in the immersion condition are approximately one order of magnitude higher than the corresponding ones measured on specimens exposed to the marine environment, except for those samples where the initial chloride content is already high (1.60%).

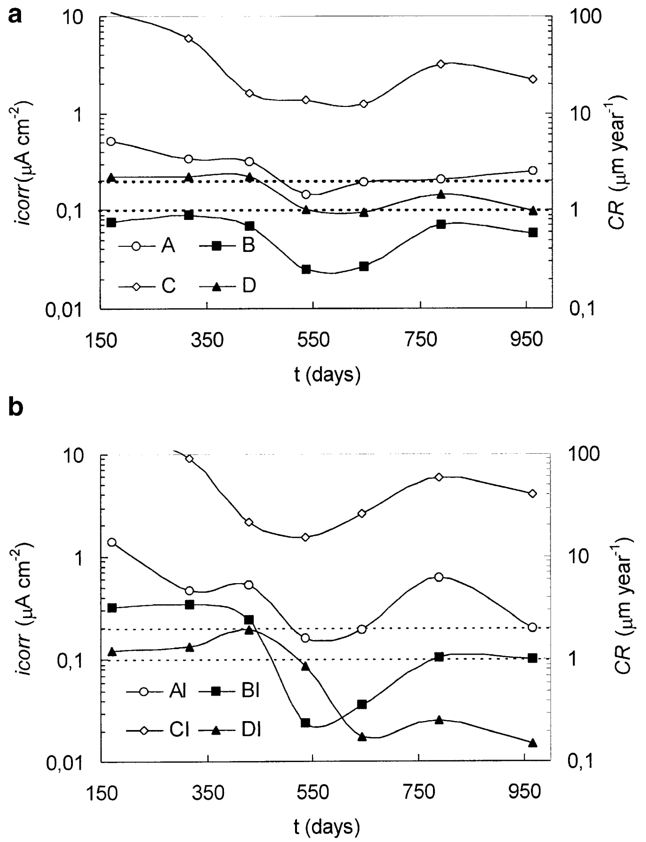

Fig. 7. Variation of the rebar corrosion current density (i_{corr}) and corrosion rate (CR) as a function of time for the four mix designs under study. Mean values for duplicate specimens are presented. Samples were exposed to the marine environment. (a) Blank specimens. (b) Treated with inhibitor.

The overall behaviour observed in the immersed specimens was similar to those observed in the marine condition. The three mix designs containing chloride ions (A, B and C) show a comparative trend in CR values, independent of the application of inhibitor. On the other hand, specimen D treated with the inhibitor presents CR values that are roughly half of the values recorded for the corresponding blank specimens (see Table 5).

These results cannot be explained by the mechanism of corrosion inhibition proposed by Welle et al. [10] on the basis of XPS measurements, for a similar inhibitor adsorbed on steel surfaces from alkaline- and chloride-containing solutions. In this paper, the inhibition effect of *N*,*N′*-dimethylaminoethanol (DMAE) is interpreted by means of the formation of a strong bond between DMAE and steel that forms a passivating film displacing ionic species from the oxidised steel surfaces, in particular chloride ions.

Therefore, the results show that the inhibitor was only effective when applied on concrete with no admixed chlorides (initial $[Cl^-] = 0.16\%$], having no beneficial effects in those mixes prepared with initial chloride contents higher than 0.43 % of cement. However, as can be seen in Fig. 4, the chloride content in sample D exposed to the marine environment can increase up to 1% after 1000 days of exposure.

3.5. Penetration of the inhibitor in concrete

In order to determine if the corrosion inhibitor penetrated the concrete cover and reached the rebar in a sufficient concentration, a qualitative test that reveals the presence of the product was performed. The method is proposed by the inhibitor manufacturer and is used to control the field application of the product. The test was performed using concrete samples extracted from the specimens exposed to the marine environment after approximately 1 year of exposure. Four concrete samples extracted from specimens AI, BI, DI (treated with the inhibitor) and A (blank) where tested. The results of the test proved that the product penetrated the concrete cover and reached the rebar surface in the three samples obtained from the treated specimens.

4. Conclusions

Under the conditions of the present study, the efficiency of the inhibitor strongly depends on the initial chloride ions concentration in concrete. The inhibitor was able to reduce the CR of steel in concrete only when the initial chloride concentration was approximately 0.2 wt.% referred to the content of cement in concrete. In this case, the inhibitor was applied to concrete having no admixed chlorides and even when samples had $w/c = 0.6$ and were exposed to a marine condition for 1000 days, the CR decreased almost one order of magnitude to values typical of steel in passive state ($CR \ll 1$ μm year^{-1}). After this period of exposure, the concentration of total chlorides raised up to approximately 1% at the rebar surface due to the incorporation of chlorides coming from the environment.

Specimens that were prepared with $w/c = 0.6$, no admixed chlorides and treated with the inhibitor show an increase in the electrical resistance measurements compared to the blank ones. This behaviour could be attributed either to an increase in the electrical resistivity of concrete or to the formation of a protective film on the rebar surface or to a combination of both factors.

On the other hand, this inhibitor effect was negligible when applied to admixtures where $a/c = 0.4$ and the total chloride concentrations initially higher than 0.43% (reaching also 1% after 1000 days of exposure to the marine environment). Thus, the product cannot be recommended for concrete prepared with raw materials contaminated with chloride ions.

The performance of this inhibitor (measured in terms of the rebar CR) depends on the quality of concrete, being better in the specimens with the highest w/c. This makes the inhibitor a promising product for those cases where low-quality concrete mixes determine the overall corrosion progress.

The use of this inhibitor under immersion conditions does not show a substantial improvement in the corrosion resistance in any of the concrete designs containing admixed chlorides. Yet, the mix design showing the lowest CR in this exposure condition is, once again, the treated one with no initially incorporated chlorides.

Further investigations are currently going on in order to determine the inhibiting mechanism, as well as the influence of other inhibitor dosages.

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