Eurocorr2005 - Investigation of Corrosion Inhibitors for Carbon Steel Used as Reinforcement of Concrete in Artificial Pore Solution

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Investigation of Corrosion Inhibitors for Carbon Steel Used as Reinforcement of Concrete in Artificial Pore Solution

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Abstract
The aim of this study was to evaluate the potential application of some chemical compounds as corrosion inhibitors for a carbon steel (CA-50) used as reinforcement of concrete in artificial pore solution. The tested compounds were sodium nitrite (1.5% in mass), hexamethylenetetramine (1.5% in mass) and benzotriazole (10^{-2} M). The techniques used in this investigation were electrochemical impedance spectroscopy (EIS), potentiodynamic polarization tests and open circuit potential measurements as a function of time. Each compound tested was added to a solution whose composition simulates that of the liquid inside the pores of concretes. To this solution was also added sodium chloride (3.5% in mass) to simulate the corrosive effects of marine atmospheres. The corrosion resistance of the carbon steel (CA-50) was evaluated in the solutions with and without the additives. A beneficial effect (corrosion resistance increase) was found for all types of inhibitors tested, but sodium nitrite and benzotriazole showed a significant inhibiting effect.

Keywords: corrosion inhibitors, durability, nitrite, hexamethylenetetramine, benzotriazole.

1. Introduction

Aggressive agents from the environments where steel reinforced concretes are used are able to penetrate through the porous structure of the concrete and upon reaching the metallic surface of the reinforcement can cause corrosion. Corrosion prevention methods, such as the use of corrosion inhibitors may however be used in order to delay the corrosion process. Many corrosion-inhibiting additives have already been tested in search for effective protection.

Corrosion inhibiting additives, as any other additives, should not change the cement characteristics, such as resistance, diffusion rate, adherence, and retraction or expansion [1]. Inhibitors need also to be compatible with the concrete. One of the advantages in the use of corrosion inhibiting additives for reinforced concrete is that they are easily added to the water mixed with cement during concrete preparation avoiding the need for skilled human resources.

Chlorides are very often the cause of corrosion in concretes due to their penetration from the exterior. In this case, the amount of inhibitor added has to be carefully controlled [2], mainly when an anodic type of inhibitor is used, once if their concentration is not enough to eliminate corrosion it can eventually accelerate it by increasing the ratio of cathodic to anodic areas exposed to the corrosive environment.

Nitrites have already been established as effective anodic inhibitors for carbon steel used in civil engineering structures [3-6]. However, there are some limitations to their use such as environmental constraints due to possible toxic effects, mechanism of inhibition (anodic type), leading to possible risky effects when not added in sufficient amounts, and also the relatively high costs of this type of additives. In search for new types of inhibitors for application in carbon steel reinforced concrete, this work was carried out. The chemical compounds tested in this study were benzotriazole, a well known inhibitor for copper, stainless steels and carbon steels in acidic environments [7-8], and also hexamethylenetetramine [9]. These two last types of additives are organic compounds that usually interact with the interface by adsorption, covering it and, consequently, acting as a mixed type inhibitor. Although benzotriazole has been largely studied as a corrosion inhibitor for stainless and carbon steels in acid media, it is not known if it also acts as a corrosion inhibitor in alkaline environments.

All the additives were added to a solution that simulates the composition of the liquid inside the pores of concretes, to which chloride was added to emulate the effects of aggressive marine environments.

2. Materials and Methods

The steel used in this investigation is the most commonly used for reinforcements in concrete (CA-50) Electrodes from this steel were prepared by epoxy resin cold mounting leaving an area corresponding to 0.63 cm^2 for exposure to the electrolyte. The exposed surface of the steel was prepared by sequential grinding with silicon carbide paper up to #600. Subsequently, the specimen was rinsed with deionized water and dried under a hot air stream.

The test solutions used in this work were: (1) 0.01N NaOH +0.05N KOH [10], called here pore solution once it simulates the chemical composition of the liquid inside the pores of concrete; (2) pore solution plus 3.5% NaCl; (3) solution as described in (2) plus 1.5% in mass of sodium nitrite, (4) solution as described in (2) plus 1.5% in mass of hexamethylenetetramine, (5) solution as described in (2) plus 10^{-2} M of benzotriazole. All reagents used for solutions preparation were of analytical grade. The test solutions were maintained at 20 ^oC under naturally aerated conditions.

After surface preparation the electrodes were immersed in the various test solutions used and the open circuit potential was measured as a function of time. Periodically (daily), electrochemical impedance spectroscopy (EIS) tests were carried out, until four days of immersion. After this period, potentiodynamic polarization tests were carried out.

A three-electrode cell arrangement was used for the electrochemical measurements, with Ag/AgCl and a platinum wire as reference and auxiliary electrodes, respectively. All potentials referred to in this work are with respect to Ag/AgCl. The polarization and EIS tests were carried out in triplicate to evaluate the tests reproducibility.

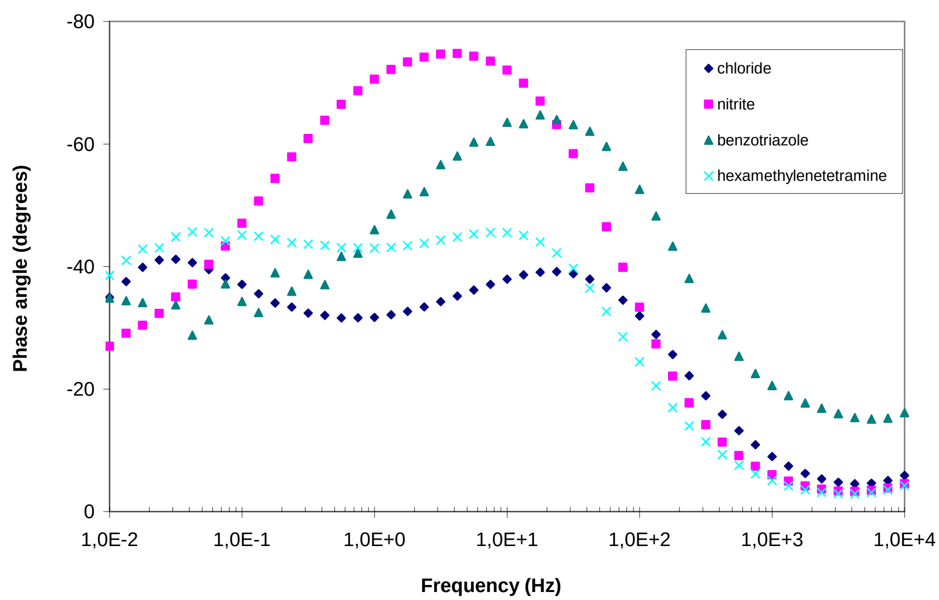
Polarization measurements were carried out using a Solartron SI 1287 potentiostat in the potential range from –0.25 V to 0.25 V versus the open circuit potential (E_{ocp}) at a scan rate of 0.5 mV/s.

The EIS tests were accomplished by means of a Solartron Model SI 1255 Frequency Response Analyzer coupled to a Princeton Applied Research (PAR) Model 273A Potentiostat/Galvanostat. The diagrams were obtained in potentiostatic mode at the corrosion potential, E_{corr}, with an ac perturbation amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz, with 8 points per decade.

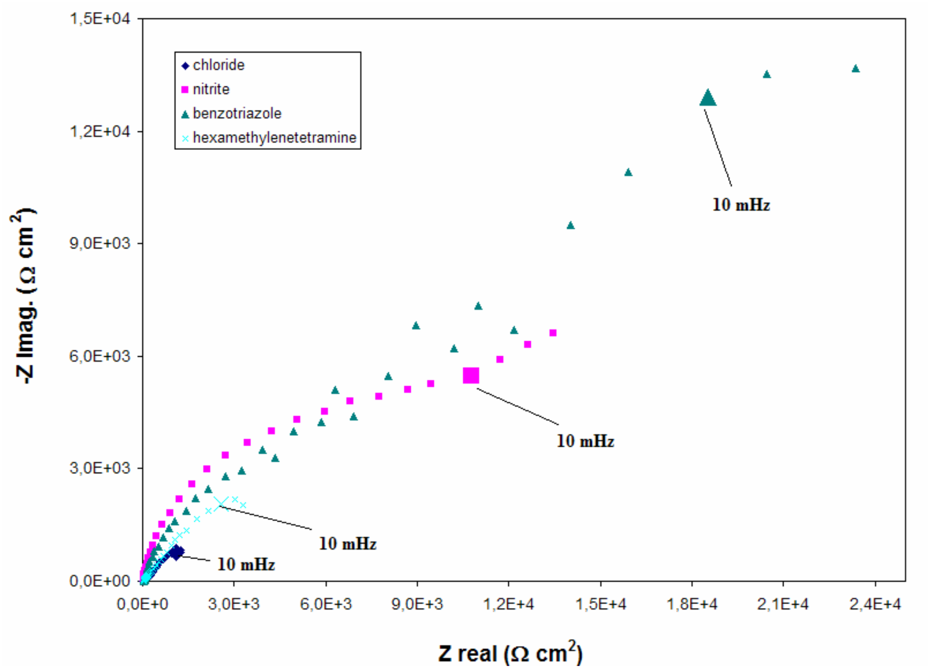
3. Results and Discussion

Figure 1 shows the EIS diagrams for the CA-50 steel used in this study after four days of immersion in all the test solutions. Two time-constants are indicated in the Bode plots of the steel in the pore solution with chloride. No significant changes were found for the results obtained in the hexamethylenetetramine containing solution and in the pore solution with chloride. These results suggest that this chemical compound does not have considerable inhibiting effect on the corrosion resistance of the CA-50 steel in the pore solution with chloride. The Bode diagrams also show more capacitive results for the steel in nitrite and benzotriazole containing solutions comparatively to the other types. The presence of two time constants is not evident in the solution with nitrite, although a shoulder at frequencies below 1 Hz could be indicative of a second one.

Comparing the EIS results for the two chemical compounds that indicated significant corrosion inhibiting effect, it can be seen that the peak related to the time constant at higher frequencies is dislocated into higher frequencies in the solution with benzotriazole comparatively to the one with nitrite. The Nyquist plots for this two last solutions show higher impedances associated to the steel immersed in the solution with benzotriazole. It is important to mention that the concentration of the two compounds that suggested inhibiting effects were significantly different. Much lower concentration of benzotriazole was used (10^{-2} M) comparatively to nitrite (1.5 mass %). This result supports even further the beneficial effect of benzotriazole as a corrosion inhibitor for carbon steel in chloride containing alkaline solutions.



(a)



(b)

Fig. 1 (a) Bode (phase angle) and (b) Nyquist diagrams for carbon steel (CA-50) in pore solution with 3.5% NaCl (reference solution), and reference solution with either hexamethylenetetramine (1.5 %), nitrite (1.5 %) or benzotriazole (10^{-2} M).

The corrosion inhibition efficiency related to the various chemical compounds tested was estimated by the inverse value of the impedance modulus (data obtained from presented in Figure 2) at 10 mHz for the solutions with and without additive. This last solution (pore solution plus 3.5 % NaCl) was used as the reference. The obtained values are shown in Table 1.

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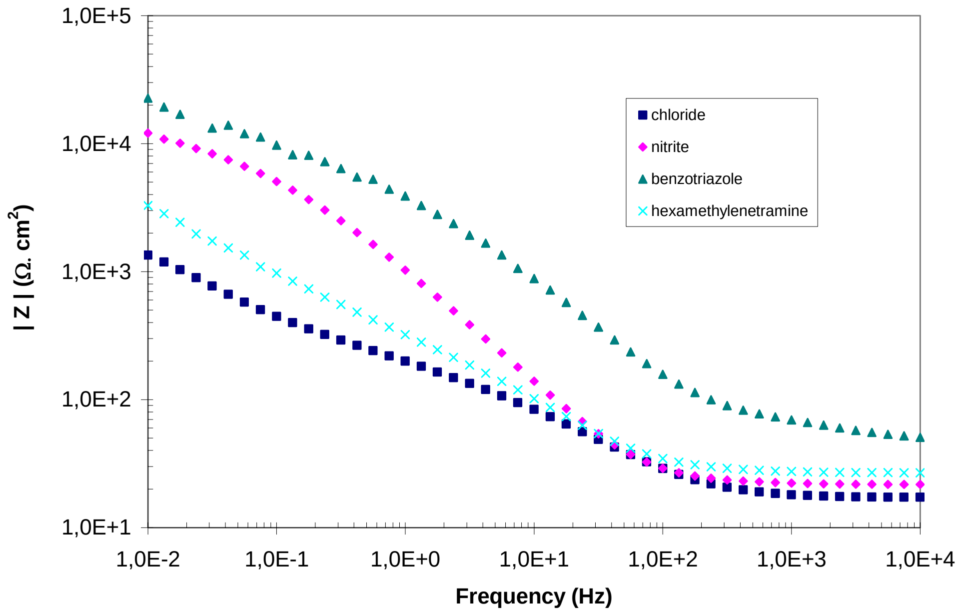

Fig. 2 Bode diagrams (Z modulus vs. log frequency) for CA-50 steel in the various solutions tested.

Table 1: Corrosion inhibition efficiency obtained from EIS data ($1/|Z|_{10mHz}$).

Solution	$1/\|Z\|_{10\ mHz}$ ($Ohm^{-1}.cm^{-2}$)	Efficiency
Reference (Pore solution + 3.5% NaCl)	$6.9\ 10^{-4}$	-
Reference + Nitrite	$8.3\ 10^{-5}$	87.9%
Reference +Benzotriazole	$4.4\ 10^{-5}$	93.6%
Reference + Hexamethylenetetramine	$3.0\ 10^{-4}$	55.5%

High efficiency values were obtained for the solutions containing either nitrite or benzotriazole, with the best efficiency value been related to this last compound (93.6%). This result suggests that benzotriazole is a potential candidate for corrosion inhibition of carbon steels in alkaline media. Table 1 also shows that hexamethylenetetramine does not act as an effective inhibitor for CA-50 steel in the solution used as reference (pore solution plus 3.5 % mass). These results were also supported by the polarization measurements, as shown in Figure 3.

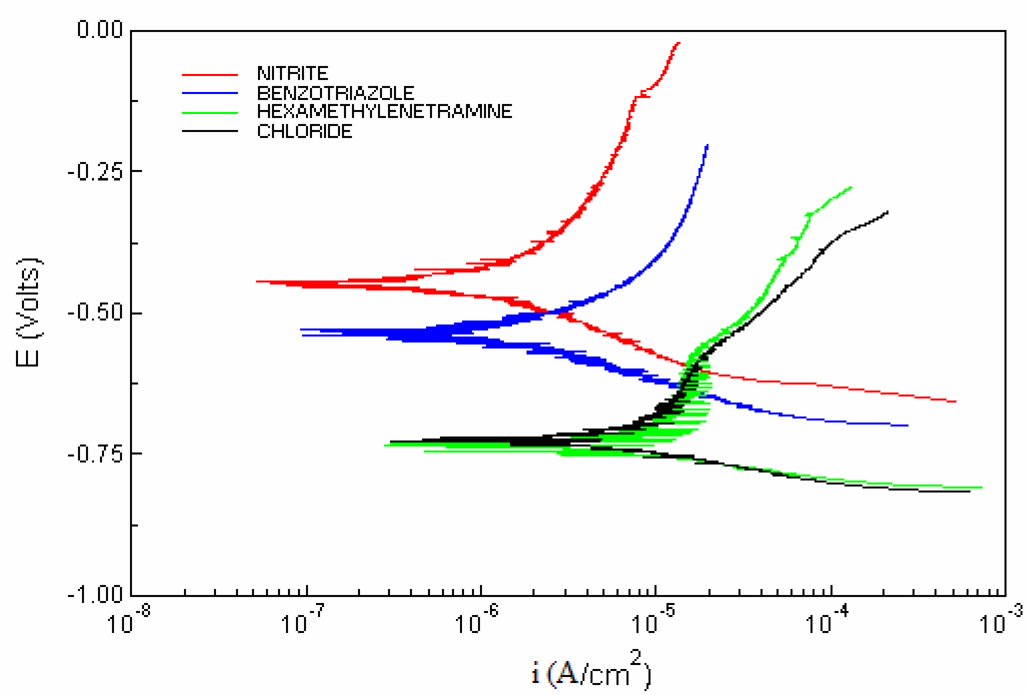

Fig. 3 Potentiodynamic polarization curves for CA-50 steel in the various test solutions. Solutions were naturally aerated and at 20 ^{o}C.

The polarization results clearly show the corrosion inhibiting effect of both additives, nitrite and benzotriazole. On the other hand, hexamethylenetetramine had no significant inhibiting effect on the polarization curve of the carbon steel used, mainly on the cathodic curve. A slight polarization of the anodic reaction of the steel at high overpotentials however resulted from the addition of hexamethylenetetramine to the reference solution. The noblest corrosion potential obtained for the steel in nitrite solution comparatively to the other solutions was expected once nitrites are well known as anodic inhibitors. The also much nobler corrosion potential associated to the solution with benzotriazole relatively to the reference one, suggests that benzotriazole had a more strong effect on the anodic reaction, although it usually acts as a mixed type of inhibitor.

4. Conclusions

The results obtained in this work strongly suggest that benzotriazole is an effective candidate for use as corrosion inhibition of the carbon steel in alkaline environments typical of those found in the pores of concretes. The highest efficiency was obtained for this additive among the ones tested. It significantly increased the impedance of the CA-50 steel in the simulated pore solution containing high chloride content. The results also suggested that benzotriazole can be used as a corrosion inhibitor in lower concentrations than that of nitrites, leading to even better efficiency than this last type of inhibitor. On the other hand, hexamethylenetramine had only a slight effect on the corrosion resistance of the carbon steel used not being considered as a potential inhibitor in the conditions tested.

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