Evaluation of benzotriazole as corrosion inhibitor for carbon steel in simulated pore solution

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ABSTRACT

In this investigation, benzotriazole (BTAH), a well known corrosion inhibitor for copper, has been evaluated as a possible corrosion inhibitor of a carbon steel (CA-50) used as reinforcement in concrete. BTAH was added to a simulated pore solution of an aged concrete with addition of 3.5 wt% NaCl to imitate marine environments. The effect of BTAH in a concentration of 1.5 wt% on the corrosion resistance of CA-50 carbon steel was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests. The improvement of the corrosion resistance due to BTAH addition was superior to that associated with nitrite in similar concentration, suggesting that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of reinforcement steel in concrete.

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1. Introduction

It is well known that steel in concrete is protected from corrosion by a microscopically thin oxide layer that is formed in the highly alkaline conditions found in the concrete pore solution. However, steel corrosion may start even in well-constructed concrete, if chlorides penetrate through the concrete and reach the steel reinforcement causing the attack of the passive film. The corrosive attack due to chloride penetration usually leads to localized corrosion causing the accelerated loss of the steel section, which might cause rapid failure of the reinforcement bar.

The addition of corrosion inhibitors is one of the corrosion prevention methods used in order to delay the corrosion process. Many corrosion-inhibiting additives have already been tested in search for effective protection [1–6]. Corrosion-inhibiting additives should not change the concrete characteristics, such as mechanical resistance and dimensional stability [7]. 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 mixing water during concrete preparation avoiding the need of highly skilled working force.

Nitrites have already been established as effective anodic inhibitors for carbon steels 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 mechanical losses

and eventually risky effects when not added in sufficient amounts, and also the relatively high costs of this type of additive. The aim of the present work was to examine another type of inhibitor for application in carbon steel reinforced concrete. The chemical compound tested was benzotriazole (BTAH), a well known inhibitor for copper and stainless steels [8,9]. Although BTAH has been largely studied as a corrosion inhibitor for stainless steels in acid environments [8,9] its effect on the corrosion resistance of carbon steels in alkaline environments has not been investigated. This investigation evaluates the effect of this compound on the corrosion of a carbon steel (CA-50) in an alkaline medium that simulates the composition of the solution inside the pores of concretes, to which chloride was added. The results for solutions containing BTAH were compared with that of similar solution with nitrites. The substitution of nitrites by BTAH would provide a significantly less toxic solution with economical advantages.

2. Experimental

2.1. Sample preparation

The chemical composition of the carbon steel (CA-50) used in this investigation is shown in Table 1.

The exposed surfaces of the carbon steel were 1 and 0.875 cm^2 for the immersion and electrochemical tests, respectively. The surface samples were prepared by sequential grinding with silicon carbide paper in the sequence #220, #320, #400 and #600. Subsequently, the electrodes were degreased in an alkaline commercial

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Table 1
Chemical composition (wt%) of carbon steel (CA-50) tested.

Element	Steel CA-50 (wt%)
Iron (Fe)	98.77
Carbon (C)	0.26
Manganese (Mn)	0.91
Phosphorus (P)	0.03
Sulfur (S)	0.026

cleaning solution, rinsed with deionized water and then dried under hot air stream.

The chemical compositions of the solutions used in this study are shown in the following. The reference solution was composed of KOH 2.8 wt% + NaOH 0.4 wt% + NaCl 3.5 wt% to simulate pore solution contaminated with NaCl.

The solution here called reference simulates the composition of the solution inside the pores of aged concretes (pH 9) to which 3.5% NaCl was added to simulate the conditions present in marine environments. Solution I corresponds to the reference solution with addition of nitrite (1.5 wt%) and solution II to the reference solution with (BTAH) (1.5 wt%) addition. Solution I and solution II were used to compare the effects of nitrite and (BTAH) on the corrosion resistance of the carbon steel investigated.

All reagents used in the solutions preparation were of analytical grade. The test solutions were quiescent and at 20 °C under naturally aerated conditions.

2.2. Immersion tests

After surface preparation some specimens were immersed in the BTAH containing solution for a period of up to 30 days to evaluate the effect of immersion in this electrolyte on the evolution of surface morphology. Periodically some specimens were removed from solution and their exposed areas were examined by optical microscopy (OM) and scanning electron microscopy (SEM). The periods corresponding to samples immersion were 1, 6, 15 and 30 days prior to each surface evaluation.

2.3. Electrochemical tests

Electrodes were prepared from carbon steel (CA-50) by epoxy resin mounting leaving an area corresponding to 0.875 cm^2 for exposure to the electrolyte. The exposed area to the electrolytes was prepared according to procedure used in the preparation of samples to immersion tests.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic anodic polarization measurements, were carried out in solutions I and II.

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. The results obtained were reproducible and no significant variation was found for a same system.

At the immersion periods specified in the electrodes were tested by using a EIS 300 frequency response analyzer and a PCI4-300 potentiostat (Gamry).

The EIS 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 10 kHz to 7.5 mHz, with 10 points per decade.

Potentiodynamic polarization tests were carried out from the corrosion potential (E_{corr}) up to an overpotential of +500 mV, using a scanning rate of 0.5 mV s^{-1}. Prior to polarization, the samples

were immersed in the solution test to evaluate the effect of the immersion time in this solution. The polarization curves were obtained after EIS tests with a PCI4-300 potentiostat (Gamry).

2.4. Raman microscopy and infrared (IR) studies for surface film characterization

Raman spectrum was obtained using a Raman Renishaw microscopy (system 3000) coupled to an Olympus optical microscope and a CCD (600 × 400 pixels) detector. IR spectra were also obtained with a NICOLET IR 200 spectrophotometer. The Raman spectrum and IR spectra were obtained from the surface area of the CA-50 steel which had been exposed to the electrolyte (1 cm^2) for 6 months, whereas the IR spectra, from a surface exposed during 90 days to the electrolyte. On both samples surfaces, a brownish product was seen, and the Raman and IR analysis was carried out on these products and on bare surfaces of the same samples.

3. Results and discussion

3.1. Surface observation by optical microscopy of CA-50 specimens with time of immersion in (BTAH) containing solution

Fig. 1 shows the evolution of the surface of the CA-50 specimens' surface with time of immersion in the BTAH containing solution (Solution II). The surface of specimens immersed in solution I did not show changes with time of immersion, due to the nitrite effect in this solution. Nitrite acts as an oxidizer leading to the formation of a thin and transparent passive layer on the CA-50 surface.

Fig. 1 shows the deposition of a layer of products on the steel surface. This layer initially is irregular and found only on few areas on the surface but it grows with time of immersion, increasing the surface coverage. For one day of immersion, few dark points on the steel surface (Fig. 1A) indicate the initiation of the film deposition. These first dark points seem to be related to the corrosive attack caused by the aggressive solution, that contains high chloride ions content. From 1 to 30 days the precipitation of a layer of brownish products increasingly spread over larger areas of the surface and at the end of the immersion period (30 days) most of the surface was covered by this layer (Fig. 1B-D). It is likely that this layer be associated to a complex formed between corrosion products from the steel surface and compounds present in the test solution, such as (BTAH).

The morphology and a semi-quantitative analysis of the layer deposited on the steel surface for periods corresponding to 15 and 30 days of immersion in solution II were analyzed by SEM and energy dispersive spectroscopy (EDS). SEM micrographs of the CA-50 steel surface after 15 and 30 days of immersion in solution II are shown in Fig. 2. The formation of the deposited layer seems to be associated to areas where corrosion has started leading to the formation of corrosion products that react with solution chemical compounds leading to the formation of a complex and, with time the formation of a precipitated layer on the steel surface. The spread of this layer apparently occurs through branches that connect regions where the deposition process has already nucleated.

SEM observation of the deposited layer on the steel surface after 15 and 30 days of immersion showed that it presents irregular and porous morphology, with cracks, whereas EDS analysis on this layer indicated that the main elements present in it are Fe, C and Cl (Fig. 2A and B).

On the other hand, the EDS spectrum obtained on the bare steel surface showed that the main peaks corresponded to iron and manganese, Fig. 3A and B, that is, elements due to the steel compo-
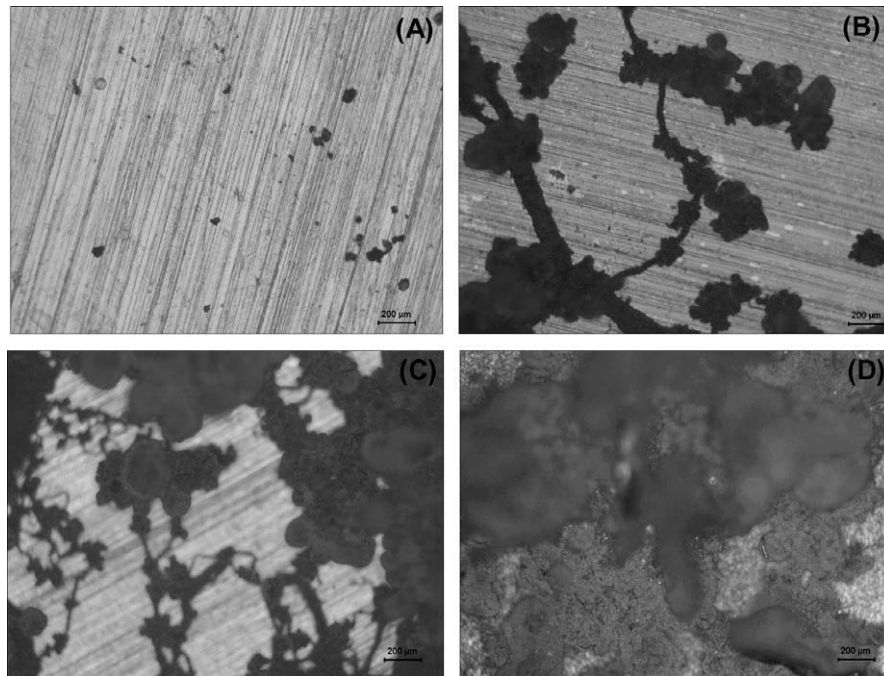
Fig. 1. Micrographs obtained by OM at various periods of immersion in the solution with (BTAH). (A) 1 day, (B) 6 days, (C) 15 days and (D) 30 days.
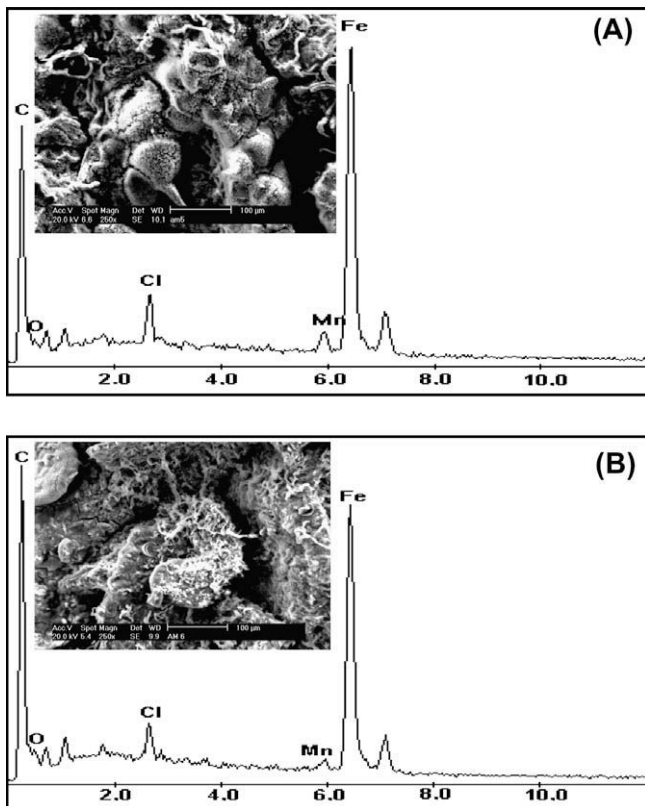

Fig. 2. SEM micrographs of CA-50 steel after (A) 15 days, and (B) 30 days, of immersion in solution II (BTAH containing solution).

sition. These results support the hypothesis that the film on the steel surface is due to a complex formed between the corrosion products and solution components, such as (BTAH) and chlorides.

3.2. Electrochemical characterization

Figs. 4 and 5 show the anodic polarization curves obtained in the various test solutions used, specifically, reference solution, solution I and solution II.

The polarization curves show the effect of the electrolyte on the CA-50 electrochemical behavior. A typically passive behavior is shown at potentials close to the corrosion potential (E_{corr}). The E_{corr} values for the specimens immersed in solution II (with BTAH) were nobler and their I_{corr} values were lower for low overpotentials than for the specimens immersed in solution I (with nitrite). On the other hand, the films obtained in the nitrite containing solution showed more stable behavior despite of their higher I_{corr} values. For this last solution, the current density increase suggesting the breakdown of the surface film occurred at higher potentials than for the specimens immersed in solution II. The breakdown potentials corresponded to approximately −0.15, −0.05 and 0.1 V, for steel specimens in solution II, reference and solution I, respectively. The lower breakdown potential associated to the specimens in solution II must be due to the characteristics of the surface film formed in this solution that showed irregularities, pores and cracks in it.

The EIS results obtained for specimens in solution II are shown in Fig. 6. The Nyquist diagrams show a highly depressed capacitive arc from 1 to 30 days of immersion likely due to the highly heterogeneous surface as it was shown in the SEM micrographs for the specimens immersed in this solution. The EIS results indicated that the impedance increased between 1 and 6 days of immersion, decreased between 6 and 15 days, and increased again between 15 and 30 days. These results reflect the high instabilities on the surface with the increasing spread of the deposited layer on the surface and its thickening with time. Thickening of the surface layer is indicated by the increase in the C peak that becomes higher than that of Fe between 15 and 30 days as the EDS spectra of Fig. 3 shows.

The evolution of the Bode phase angle diagrams with time show that from 1 to 6 days the angle peak at frequencies in the 10^1–10^0 Hz range increases and moves into lower frequencies probably
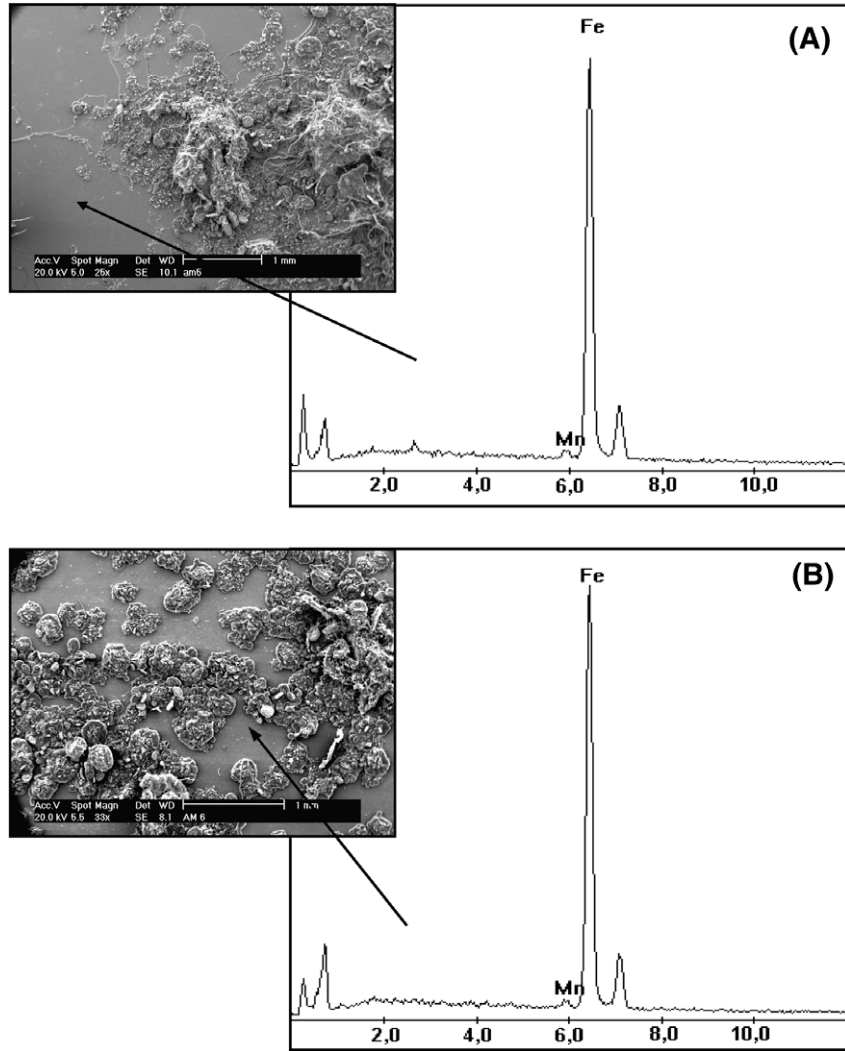
Fig. 3. SEM micrographs and EDS analysis of the metal base after (A) 15 days and (B) 30 days of immersion in solution II.
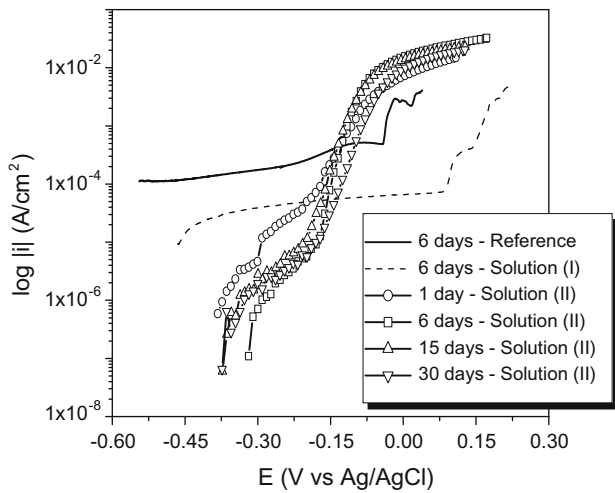

Fig. 4. Anodic polarization curves obtained in the various test solutions for 6 days of immersion and for solution II (with BTAH) at increasing immersion periods.
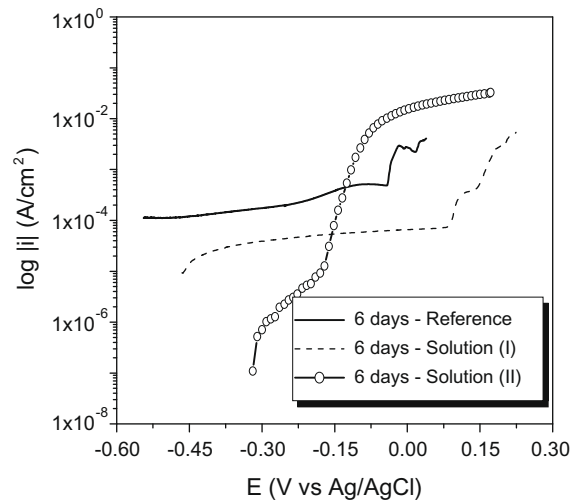

Fig. 5. Anodic polarization curves obtained in the various test solutions for 6 days of immersion.

due to the increasing coverage of the anodic areas with the deposited layer and also to the thickening of this layer. Between 6 and 15 days of test, however the phase angle peak decreases and it

moves into higher frequencies. This could be associated to the increasing porosity and the cracks development in this layer as it thickens with time, favoring the access of electrolyte species and
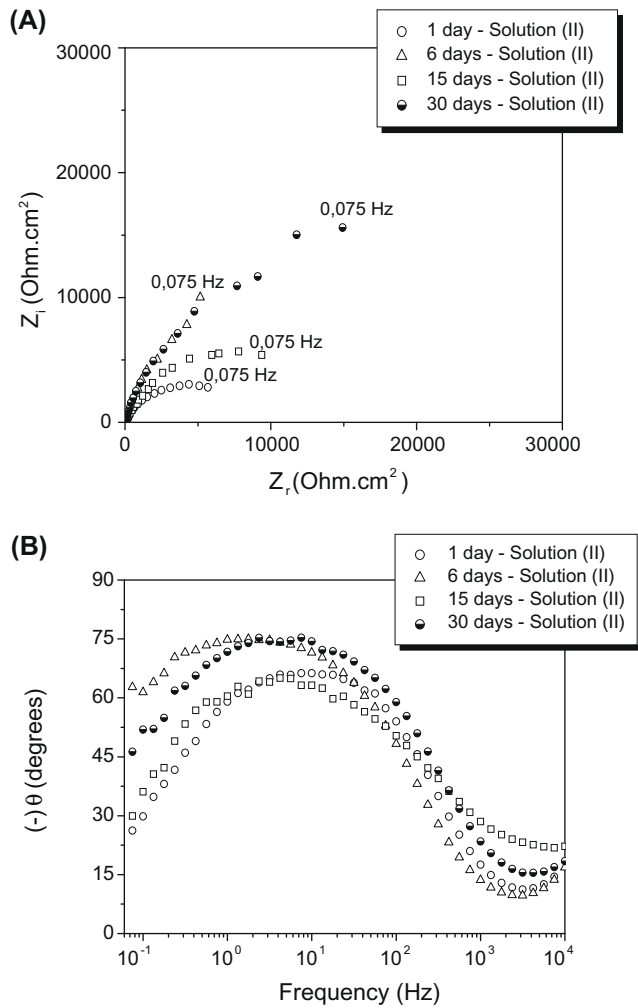
Fig. 6. Nyquist (A) and Bode phase angle (B) diagrams of CA-50 steel specimens immersed in solution with BTAH (solution II).

also the charge transfer process increasing its kinetics. The increasing kinetics of charge transfer processes, on the other hand, will cause the increasing formation of corrosion products and consequently the more products will deposit causing the temporary blockage of the defective areas that facilitate the aggressive species to the substrate. The results indicate that the presence of the additive BTAH in the solution has a auto-repairing effect on the defective areas of the deposited layer once the corrosion process starts at the bare metallic surface exposed on their base.

A comparison on the effects of the additives BTAH and nitrite on the corrosion behavior of the CA-50 steel specimens was carried out for 6 days of immersion by EIS. The results in the reference solution were also used for comparison reasons and these are shown in Fig. 7. The EIS results show much larger impedances related to the samples immersed in BTAH containing solution comparatively to the nitrite containing one.

Although the effect of BTAH on compressive strength has not been investigated in the present study, prior work carried out in our laboratory using an organic additive (tannin) in similar concentrations to the ones used in this investigation (1.5 wt%), found no effect on the concrete compressive strength.

3.3. Characterization of the layer formed on the CA-50 steel surface

The characterization of the film formed on the CA-50 steel surface was carried out by Raman spectroscopy and infrared spectros-
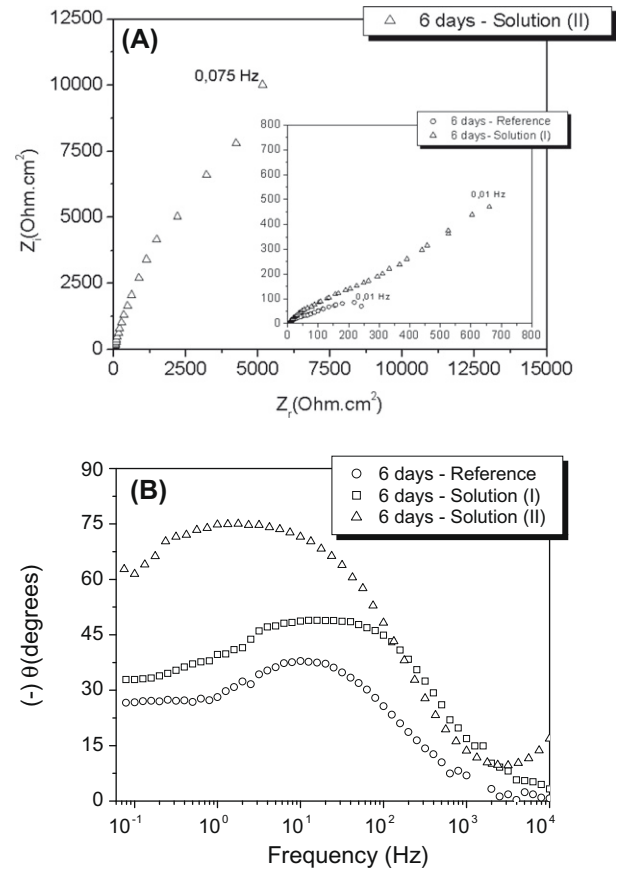

Fig. 7. Nyquist (A) and Bode phase angle (B) diagrams of CA-50 steel after 6 days of immersion in the reference solution, solution I (with nitrite) and solution II (with BTAH).
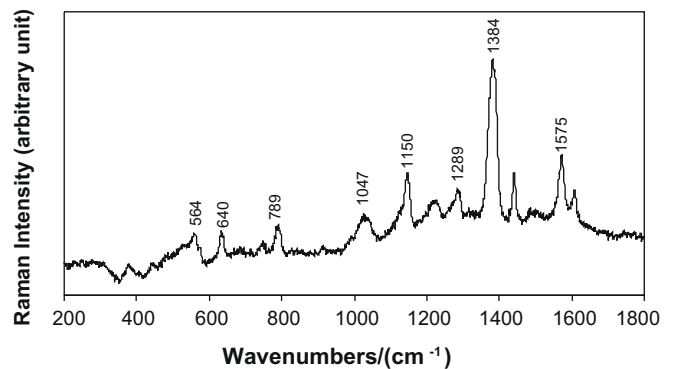

Fig. 8. Raman spectrum of the deposited layer on the CA-50 steel after 30 days of immersion in BTAH containing solution (Solution II).

Table 2
Main peaks found in the Raman spectrum obtained at the layer deposited on the CA-50 steel.

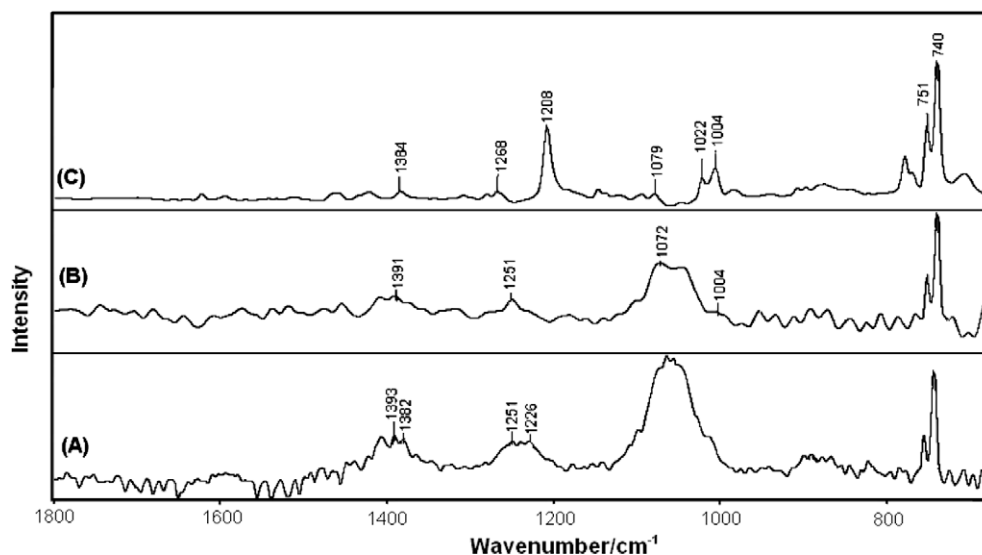| Complex $Fe_n(BTA)_m$ (cm^{-1})	Attribution
564	Triazole ring bend
640	Triazole ring torsion
789	Benzene ring breathing
1047	Triazole + benzene ring mode
1150	CH in-plane bending
1289	νSkeletal + CH bending
1384	Benzene + triazole ring stretching
1575	Benzene ring stretching

Fig. 9. Infrared spectrum of two regions of the CA-50 steel surface treated in the solution with BTAH (A) and (B) and of the benzotriazole compound (C).

copy (IR). The Raman spectrum obtained on the layer deposited on the steel surface is shown in Fig. 8. The peaks identified in the Raman spectrum were compared with results published in the literature [10,11] and they suggested the presence of a complex film (Fe_nBTA_m) formed by immersion in solution II.

The formation of a complex with benzotriazole depends on the electrode potential, and the solution pH and concentration. The pH of solution II s is alkaline suggesting that the benzotriazole must be found BTA^-, that is, desprotonated. The lack of the 1096 cm^{-1} peak in the Raman spectrum, that is typical of the N–H bonding vibration supports this hypothesis. Another evidence for the BTA^- presence in the complex layer formed on the steel surface is that the 1201 cm^{-1} peak, typical of the N–H bonding coupled to the triazolic ring, was not found in the spectrum [10,11,12–19]. The benzotriazole presence on the steel surface was however confirmed by the main peaks detected in the Raman spectrum which are listed in Table 2.

It is possible that chloride ions take part in the complex composition as $[Fe_n(Cl)_p(BTA)_m]$ and their adsorption might occur by coordination of the pairs of free electrons from nitrogen atoms with iron [10]. The EDS results presented in Fig. 2 support the formation of a chloride containing complex as $[Fe_n(Cl)_p(BTA)_m]$ by the high Cl peak found in the EDS spectrum.

Fig. 9 shows the IR spectrum from two regions of the brownish product deposited on the CA-50 steel formed in the (BTAH) containing solution (solution II).

The IR spectrum indicated as (C) corresponds to the benzotriazole used as additive in the solution whereas the (A) and (B) spectra were obtained from areas with deposited brownish products. These results evidenced the presence of benzotriazole on the CA-50 steel surface, showing similar bands characteristics of benzotriazole on all obtained spectra. The bands close to 779 cm^{-1} are typical of the benzene ring vibration and the band near to 1390 cm^{-1} is characteristic of the aromatic and the triazole rings stretching vibration. The band at 1208 cm^{-1} seen in the (C) spectrum is typical of the triazole ring breathing and this is masked on the (A) and (B) spectra, due to the adsorption of benzotriazole to the metallic surface. The band at 1070 cm^{-1} was detected only on the (A) and (B) spectra and it has been associated in the literature to Fe–O–Fe [20], showing the participation of oxide products resulting from corrosion in the film deposited on the CA-50 surface. Therefore, it can be concluded that the IR results supported those obtained by Raman microscopy and also

the surface analysis by SEM and optical microscopy on the CA-50 steel surface.

4. Conclusions

The addition of BTAH into a simulated chloride-contaminated pore solution caused a significant increase in the corrosion resistance of the carbon steel (CA-50). The improvement of corrosion resistance by the BTAH (1.5 wt%) addition was superior to that associated to the addition of nitrite (1.5 wt%) to the electrolyte, suggesting that BTAH is a potentially attractive alternative to nitrites for inhibiting corrosion of steel reinforcement in concrete. The increase in corrosion resistance was associated with the formation of a complex layer of $[Fe_n(Cl)_p(BTA)_m]$ that spreads over the steel surface with immersion time acting as a partial barrier to the access of environment aggressive species to the metallic substrate.

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