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The application of electrochemical impedance spectroscopy to determine the long-term effectiveness of corrosion inhibitors for steel in concrete

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Abstract

The excellent corrosion resistance of steel in reinforced concrete is decreased in the presence of chloride ingress the carbonation of this cover.

The use of inhibitors is one of several possible methods to protect rebar from corrosion. The most common practice is their addition together with the mixing water of concrete.

In this work, we have studied the effect of two "commercial" inhibitors: calcium nitrate and alkanolamine on the corrosion resistance of reinforcing steel, as function of time.

The concrete tested was made with 400 kg m^{-3} Portland cement, which has a high resistance to sulphate, and the water–cement ratio was equal to 0.4. Inhibitors were introduced in fresh concrete mix at different contents. Tests were conducted with reinforced concrete specimens.

Specimens were immersed in salt solution (0.5 M of NaCl) for three years. During this period, the condition of steel was monitored each year, with measuring zero-current potential and electrochemical impedance spectroscopy (EIS).

It appears that alkanolamine based inhibitor has not a negative effect on the bulk concrete cover. However, calcium nitrate inhibitor does not improve the concrete properties. These "commercial" inhibitors are not effective, when chloride is present on the steel–concrete interface.

Keywords: Steel reinforcement; Concrete; Corrosion; Inhibitor; EIS technique

1. Introduction

In sound concrete, with pH of about 12, a passivation film protects embedded steels. But, sometimes, reinforcing steel corrodes after chloride ions or carbon dioxide penetrate the concrete cover. During the past 15 years, corrosion-inhibiting admixtures (CIAs) have been increasingly popular for protecting of reinforced concrete components of structures from damage induced by chloride. However, there remains a considerable debate recently about the benefits of CIAs in concrete. At the present time, there are only few corrosion inhibitors admixtures are available on the Tunisian market. Among them are: calcium nitrite [1], calcium nitrate [2], Ferrogard 901 and MCI 2000 [3].

A variety of testing methods to assess the performance of CIA have been reported in the literature [4,5], ranging from tests in simulated pore solutions to long-term exposures of concrete slabs. The protection mechanisms of "commercial" inhibitors are also described in several papers [6–8]. But no data exist on the use of inhibitors in Tunisian concrete structures.

This study was carried out to evaluate the long-term effectiveness of alkanolamine (Ferrogard 901) and calcium nitrate (CNTQ) for inhibiting corrosion in concrete. The method, which was used was electrochemical impedance spectroscopy (EIS), which is a powerful and general technique suitable for characterizing the electrochemical processes in inhomogeneous or multiphase materials. It can estimate a steady-state corrosion rate and subsequently the efficiency of corrosion inhibitors.

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2. Experimental

2.1. Materials used

Reinforced concrete specimens were prisms, measuring 40 × 40 × 160 mm^3 (Fig. 1(a)). Reinforcement was a cylindrical plain carbon steel (C = 0.22%) bar, 6.5 mm in diameter and 120 mm long. Brushing, before being placed in concrete mould cleaned it. A copper wire was welded in its middle for connecting it to the electric circuit (Fig. 1(b)). This weld and the sides of the rebar were protected with epoxy resin. Concrete cover was about 20 mm.

Specimens were made of Portland cement with a high resistance to sulphate referred as CPHRS. The water to cement ratio was equal to 0.4. Concrete proportion is given in Table 1. After its placing in mould, concrete was compacted by vibrating.

The inhibitors tested were "commercial" calcium nitrate and alkanolamine which were added into concrete during its mixing. The content of calcium nitrate based inhibitor was equal to 0% (reference specimens), 2%, 4% and 6% against cement weight. Alkanolamine content was equal to 3, 6 and 9 l m^{-3} of concrete.

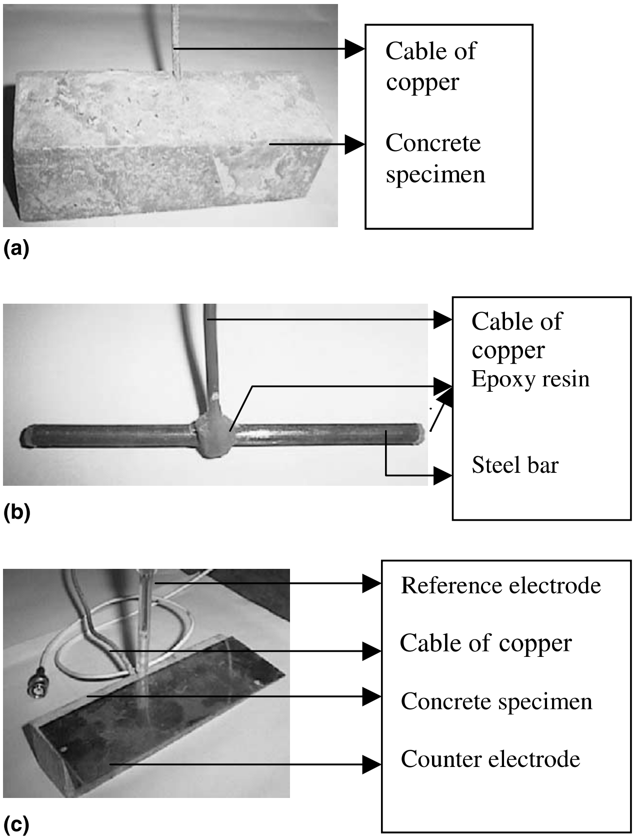

Fig. 1. Specimens used in this study: (a) concrete specimen; (b) steel reinforcement; (c) cell used for electrochemical tests.

Table 1
Concrete proportion

Component	Portland cement	Sand	Gravel
Maximum diameter (mm)		5	8
Content (kg m^{-3})	400	635	1290

2.2. Ageing of specimens

After curing, specimens were placed in a tight vessel containing 3 l of solution, with no possibility of evaporation. Solution was either distilled water (reference solution) or sodium chloride (0.5 M) solution. Copper wire, which connected the reinforcing steel to the electric circuit, passed tightly through the vessel top.

This ageing by immersion in salt solution, lasted three years. During this period, the condition of steel was monitored each year, with measuring zero-current potential and electrochemical impedance spectroscopy.

2.3. EIS measurements

EIS deals with polarising reinforcing steel with a weak alternate current (AC) against a counter-electrode, and with measuring steel potential E, against a reference electrode. The counter-electrode used was a stainless steel (18% Ni, 10% Cr) plate and the reference electrode was a saturated calomel (SCE). For plotting diagram of AC electrochemical impedance at zero-current (open circuit) potential, specimens were taken out of the solution and the counter-electrode and reference were placed on the surface (Fig. 1(c)).

The equipment used included:

- A potentiostat (Solartron SI 1286).
- An analyser of transfer function (Solartron FRA SI 1250) and a filter (Kemo VBF8).
- A PC computer with FRACOM software for plotting impedance by controlling the analyser of transfer function and a SIMPLEX software for modelling experimental data by an "equivalent electric circuit". Plotting on the same graph the experimental and calculated Nyquist diagrams checked the validity of the calculated results.

Steel was polarised at ±10 mV around its zero-current potential. Frequency was ranging between 65 kHz and 10 mHz, with five frequency values per decade.

3. Results interpretation

3.1. Zero-current potential

Zero-current (open circuit) potential E_c of reinforcing steel was measured each year, before applying EIS test.

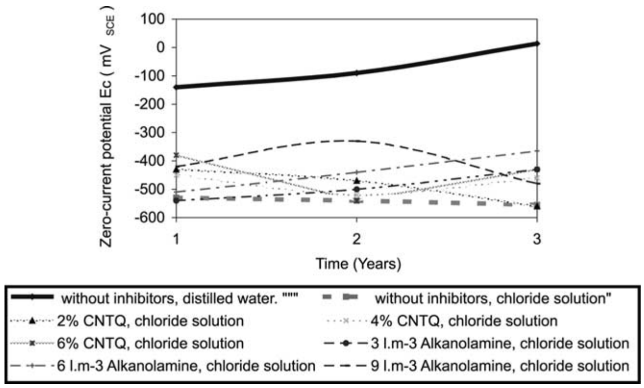

Fig. 2. Zero-current potential versus time.

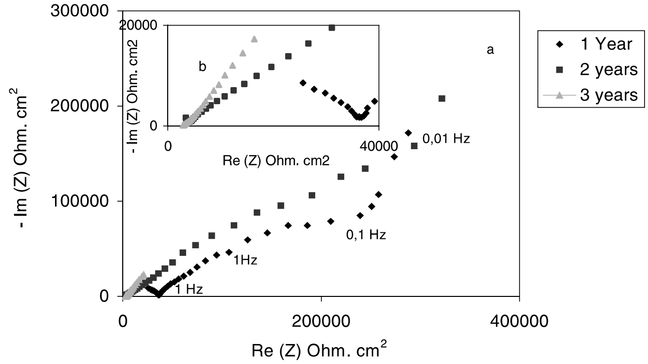

Fig. 3. Nyquist diagrams of steel bars embedded in concrete containing 6% of “calcium nitrate” against cement weight and immersed in distilled water: (a) complete diagram; (b) high frequency arcs.

The results obtained are shown in Fig. 2. With control specimens, which were free from inhibitor, the potential was very and permanently negative when specimen was in chloride solution. It was less negative when specimen was in distilled water. It means that since the first year, reinforcing steel was depassivated by chloride ions and corrosion occurred.

This figure also shows the effect of inhibitor on the open circuit potential of reinforced concrete specimens, which were immersed in chloride solution. The values of corrosion potentials are less negative or similar to those of control specimens, which were immersed in the same aggressive solution. According to Stratfull [9], when its corrosion potential value is more negative than -270 $\mathrm{mV_{SCE}}$, steel in concrete is corroding.

3.2. EIS

3.2.1. Experimental results

EIS studied the long-term behaviour of steel in concrete (without and with inhibitor). The Nyquist plots shows that the steel–concrete interface response contains two or three loops (capacitive arcs with or without an inductive loop), whose centres lie below the real axis and which are more or less separated. Figs. 3–9 give typical diagrams for the different period of immersion time.

The fitting of EIS Nyquist plots formed of two or three capacitive arcs was made according to the electric circuit illustrated in Fig. 10(a). Figs. 11 and 12 show the comparison between experimental and calculated typical

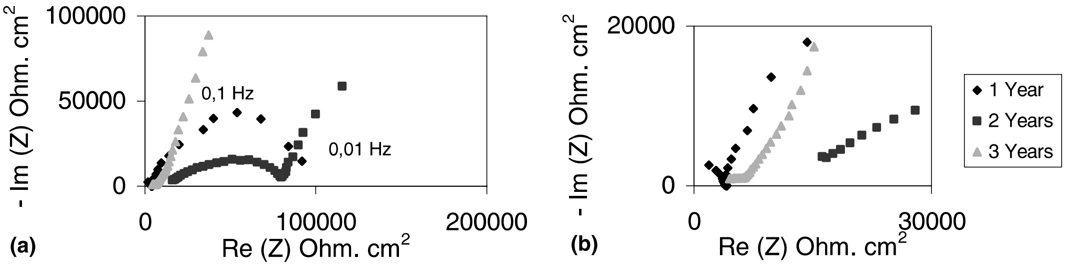

Fig. 4. Nyquist diagrams of steel bars embedded in concrete containing 3 l $\mathrm{m^{-3}}$ of “alkanolamine” and immersed in distilled water: (a) complete diagram; (b) high frequency arcs.

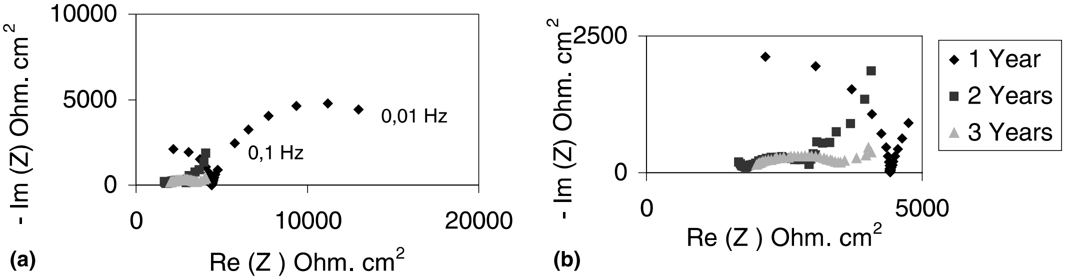

Fig. 5. Nyquist diagrams of steel embedded in concrete without inhibitors and immersed in 0.5 M NaCl solution: (a) complete diagram; (b) high frequency arcs.

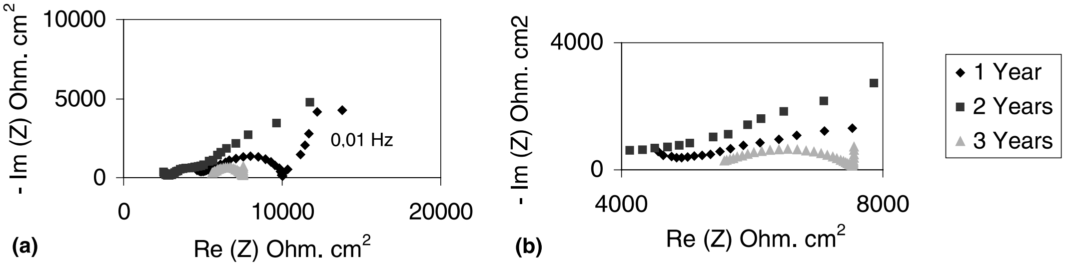

Fig. 6. Nyquist diagrams of steel embedded in concrete containing 2% of "calcium nitrate" against cement weight and immersed in 0.5 M NaCl solution: (a) complete diagram; (b) high frequency arcs.

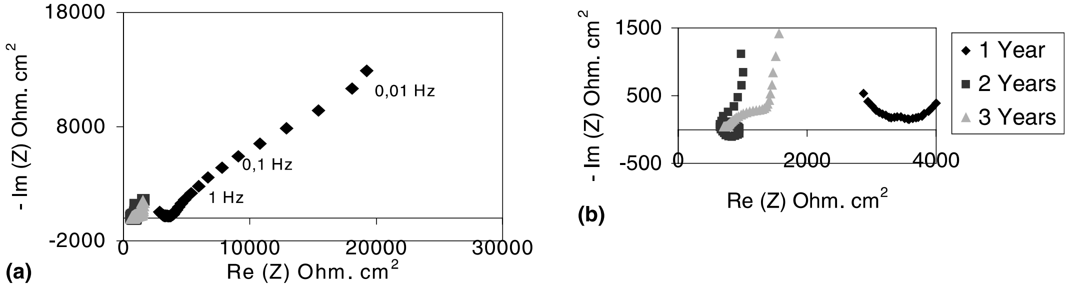

Fig. 7. Nyquist diagrams of steel bars embedded in concrete containing 6% of "calcium nitrate" against cement weight and immersed in 0.5 M NaCl: (a) complete diagram; (b) high frequency arcs.

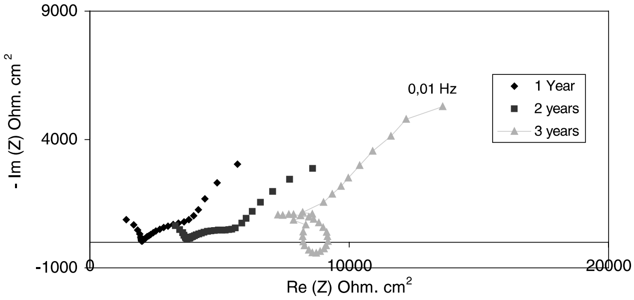

Fig. 8. Nyquist diagrams of steel bars embedded in concrete containing 3 l m^{-3} of "alkanolamine" and immersed in 0.5 M NaCl.

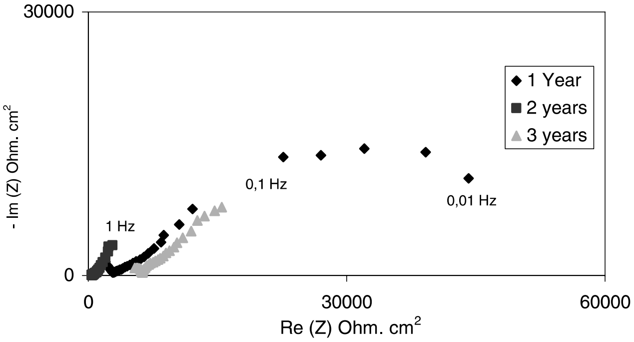

Fig. 9. Nyquist diagrams of steel bars embedded in concrete containing 6 l m^{-3} of "alkanolamine" and immersed in 0.5 M NaCl solution.

EIS Nyquist plots. The circuit shown in Fig. 10(b) was used to simulate the EIS plots containing an inductive loop. Fig. 13 shows the results of the simulations. It is being noticed that the best fitting was obtained by introducing a symmetrical Cole–Cole distribution on the time constants. In all cases, a discrepancy, which was less than 5%, was observed between experimental and calculated values of the impedance. Thus, these electric models describe the steel–concrete interface, which is represented in Fig. 10(c), and subsequently the experimental diagrams can be used to determine the values of the various elements in the electric circuits of Figs. 10(a) and (b).

The two models are composed of the electrolyte resistance R0, in series with other elements, which are:

- A resistance R1 that corresponds to the high frequency arc. It is related to the resistance of products formed in cement pores around steel reinforcement [10–13]. The corresponding capacitance values (C1) obtained from all diagrams are in the order of 1–10 μF cm^{-2}. These values are not compatible with an interfacial film [14]. According to [15,16], this order of magnitude is indicative of bulk effects and the high frequency process is related with the concrete properties [17].
- A resistance R2 that is the diameter of the intermediate arc. In most of spectra, this arc was a capacitive one. The corresponding calculated capacitor C2 has a value in the 1–10 μF cm^{-2} range and does not

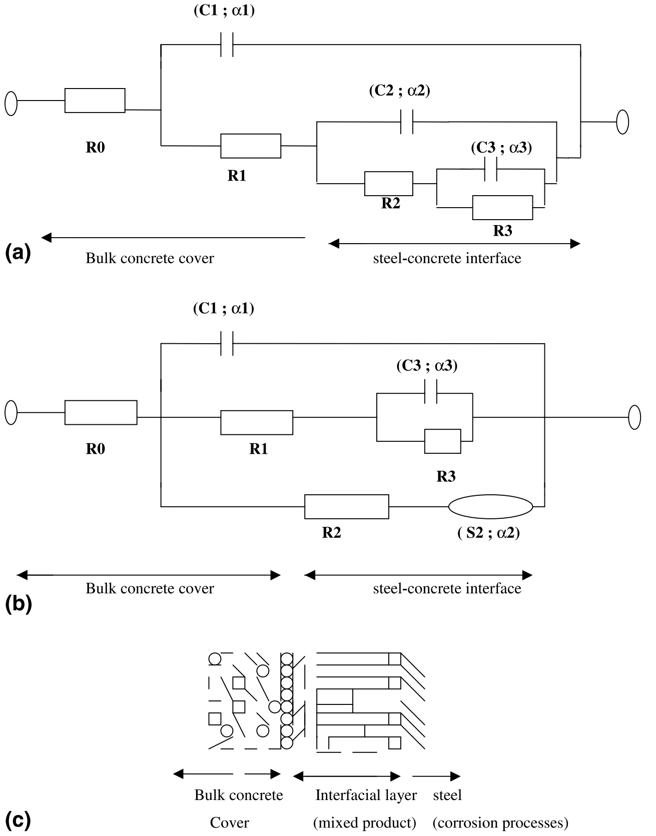

Fig. 10. Electric circuit models of the concrete–steel interface: (a) electric circuit for diagrams containing capacitive arcs; (b) electric circuit for diagrams containing an inductive loop; (c) schematic representation of the steel–concrete interface.

change significantly with time. The magnitude of this capacitance is lower than the double layer capacitance. So, this arc is not indicative of a charge transfer process but is due to a surface film and R2 deals with its ionic resistance.

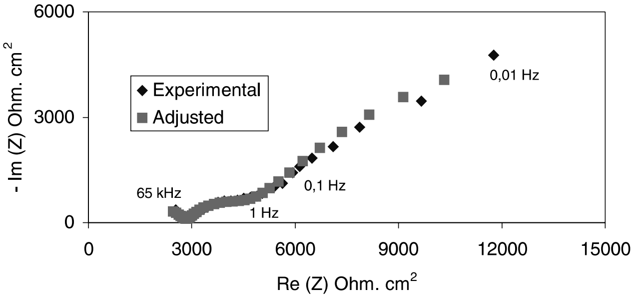

Fig. 12. Experimental and fitted diagram. Steel bars embedded in concrete containing 2% of calcium nitrate against cement weight and immersed for two years in 0.5 M NaCl solution.

These elements R2 and C2 are absent in diagrams corresponding to control specimens immersed in distilled water, during only 1 year. The capacitance C2 was converted to an inductance S2 with specimens containing 4% or 6% of nitrate (per weight of cement) and immersed for 2 years in chloride solution and with specimens containing 3 l m^{-3} of alkanolamine and aged 3 years in the same aggressive solution. Its meaning remains unclear.

- A resistance R3 that corresponds to the low frequency arc. This resistance was used to estimate the polarisation resistance of the steel. The calculated value of C3 capacitance is ranging between 0.2 and 100 mF cm^{-2}. This capacitance is high to be associated with a double layer capacitance. So, it would be possible to ascribe the low frequency loop to a charge transfer process in combination with a mass transport process [18]. This Faradic process takes place on steel surface uncovered by the interfacial film.

3.2.2. Discussion of the EIS results

For studying the long-term effectiveness of corrosion inhibitors for steel in concrete, by using specimens aged

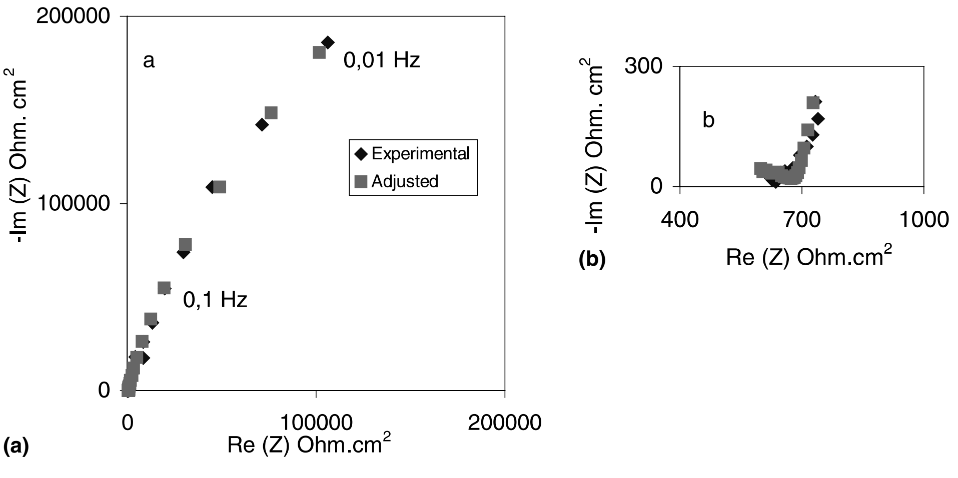

Fig. 11. Experimental and fitted diagram. Steel bars embedded in concrete and immersed for one year in water: (a) complete diagram; (b) high frequency arc.

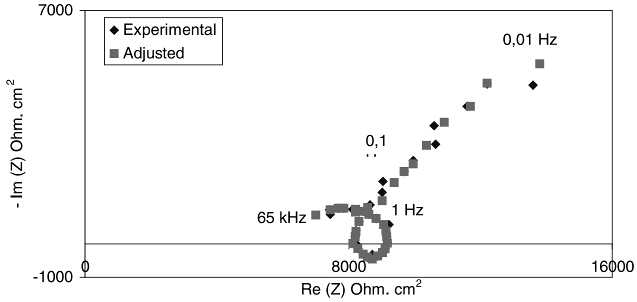

Fig. 13. Experimental and fitted diagram. Steel bars embedded in concrete containing 3 l m^{-3} of alkanolamine and immersed for 3 years in 0.5 M NaCl solution.

in distilled water or in chloride solution, the fitted parameters, R0, R1, R2 and R3 of EIS Nyquist diagrams were considered.

3.2.2.1. Properties of concrete cover. Fig. 14 shows the change of the resistances R0 and R1 versus time, corresponding to specimens free from inhibitor and immersed either in distilled water or in chloride solution. These resistances increased intensely for specimens immersed in distilled water, and slightly for those immersed in aggressive solution. It can be explained by the fact that for long immersion time, hydrating cement products decrease the porosity of concrete and increase concrete resistivity. The lower values of R0 and R1 for specimens immersed in chloride solution, are related to the presence of dissolved ions in the concrete pore solution.

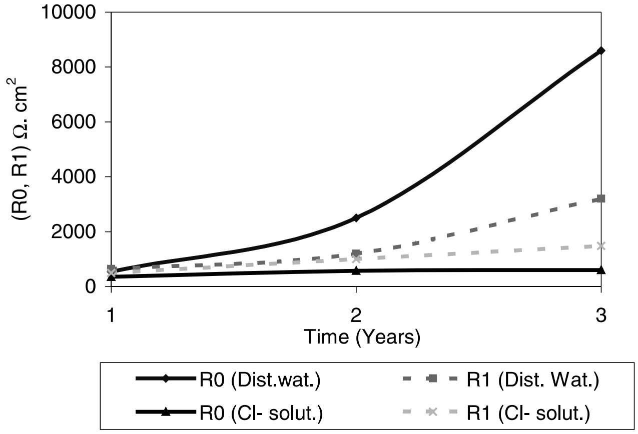

Fig. 14. Evolution of R0 and R1 versus time for control specimens.

The effect of calcium nitrate on the resistances R0 and R1 is shown in Fig. 15. These resistances are higher with nitrate than without inhibitor at least after first year immersion. This may indicate a reduction of the solubility of some cements components such us $Ca(OH)_2$ [19]. After, R0 and R1 tend to decrease with time (Fig. 15(a) for water and Fig. 15(b) for chloride solution). This is possibly due to the ageing or to the disappearance of the inhibitor.

The change of the resistances R0 and R1 versus time, for specimens containing alkanolamine and immersed in water is given in Fig. 16(a). These resistances reach maximum values after 2 years of immersion; then, they decrease and become similar to those, which were determined after 1 year of immersion. The increase of these resistances can be due to the introduction of high resistivity organic compound in concrete [20]. The further decrease of R0 and R1 values could be due to the ageing of alkanolamine, which would produce soluble ions.

For specimens, which contained alkanolamine and were immersed in NaCl solution, the values of resistances R0 and R1 saved the same values or increased slightly with time (Fig. 16(b)).

3.2.2.2. Action of the inhibitors on steel–concrete interface. Fig. 17 gives the change of the resistances R2 and R3 with time for specimens free from inhibitors and

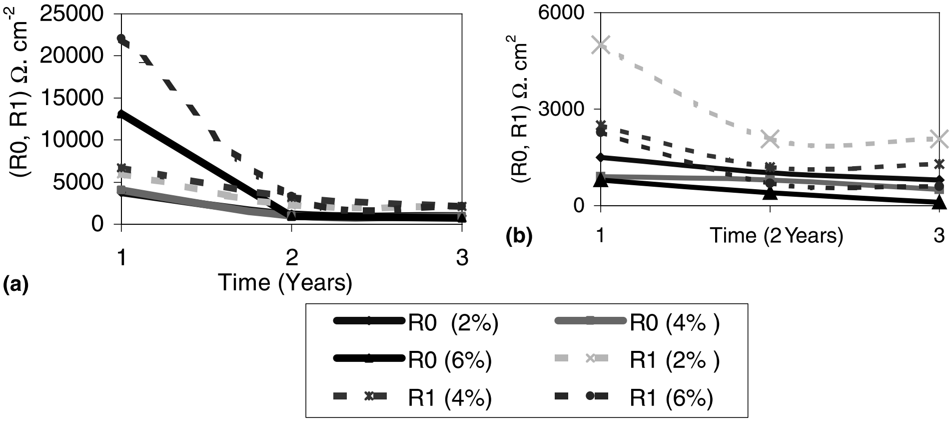

Fig. 15. Evolution of R0 and R1 versus time. Specimens containing calcium nitrate (against cement weight): (a) water immersion; (b) chloride immersion.

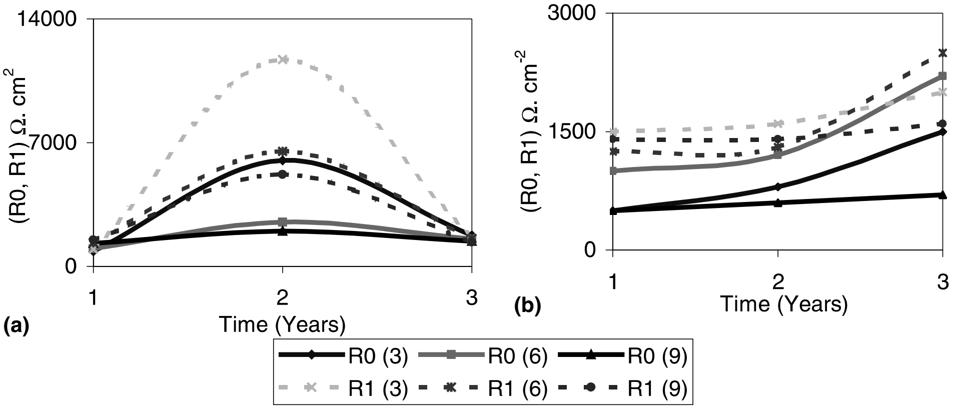

Fig. 16. Evolution of R0 and R1 versus time for control specimens containing alkanolamine (l m^{-3} of concrete): (a) water immersion; (b) chloride immersion.

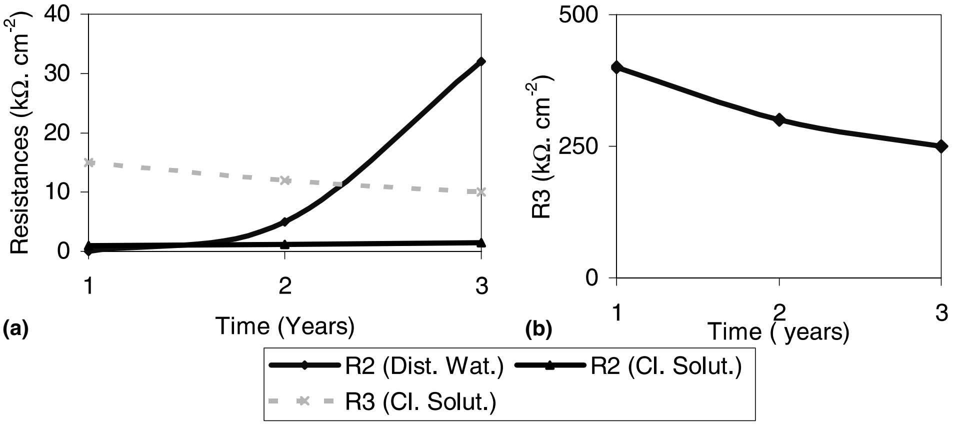

Fig. 17. Evolution of R2 and R3 versus time for control specimens: (a) water (R2) and chloride solution (R2, R3); (b) water (R3).

immersed either in water or in chloride solution. For specimens immersed in water, an important increase of R2 and a slight decrease of R3 are observed. This means that reaction products with a high resistivity are formed on the steel surface. In the presence of chloride, the values of R2 and R3 are very low. This means that steel is corroding.

Fig. 18 gives the change of the resistances R2 and R3 for specimens containing calcium nitrate, and immersed either in water or in chloride solution. Figs. 18(a) and (b) corresponding to immersion in water, show that resistance R2 decreases and R3 increases. It means, that inhibitor ions are present at the interfacial layer and are able to decrease the corrosion rate. Figs. 18(c) and (d) corresponding to immersion in chloride solution show that resistances R2 and R3 decrease with time. This indicates that this inhibitor does not prevent corrosion process to occur, when chloride is present.

Fig. 19 gives the changes of resistances R2 and R3 for specimens, which contained alkanolamine and were immersed in tested solutions. Fig. 19(a) corresponding to immersion in water, shows that resistances R2, R0 and R1 (Fig. 16(a)) change in the same way. For the same solution the value of resistance R3 increases slightly with time (Fig. 19(b)). It means that an unstable interfacial layer is formed on steel surface, but it is able to keep the interface under a passive state.

For specimens immersed in NaCl solution, the values of R2 and R3 resistances decrease versus time (Figs. 19(c) and (d)). So, when chloride ions are present at steel–concrete interface, the products, which are formed, are no more protective: steel corrosion occurs.

4. Conclusion

From the results of this study some concluding remarks are drawn:

- Under the experimental conditions of this study, control specimens, without inhibitor, corroded. So, the effectiveness of the two inhibitors tested may be assessed.

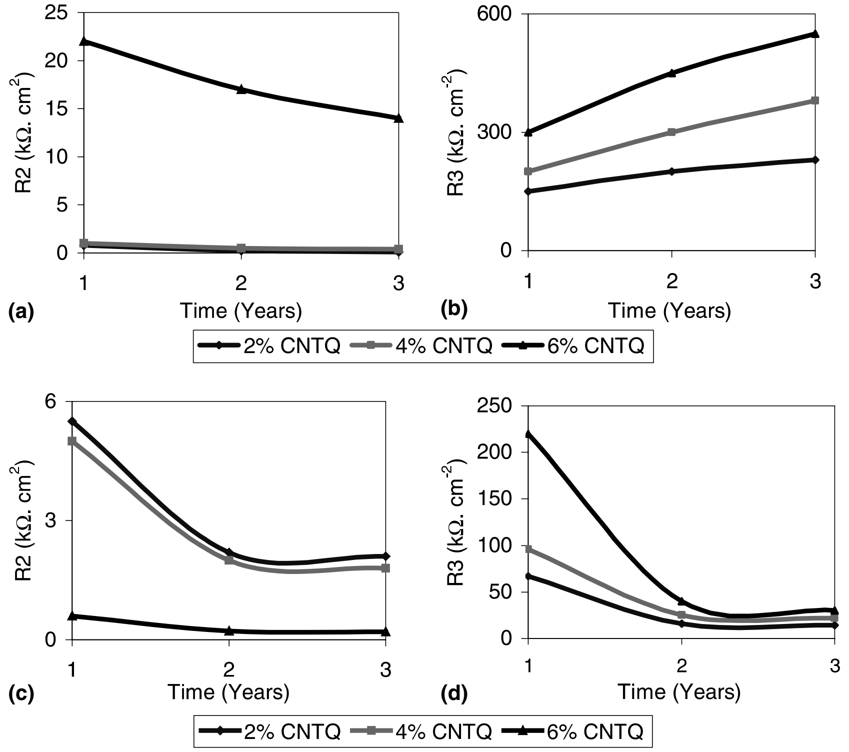

Fig. 18. Evolution of resistances R2 and R3 versus time for specimens containing calcium nitrate: (a) water (R2); (b) water (R3); (c) chloride solution (R2); (d) chloride solution (R3).

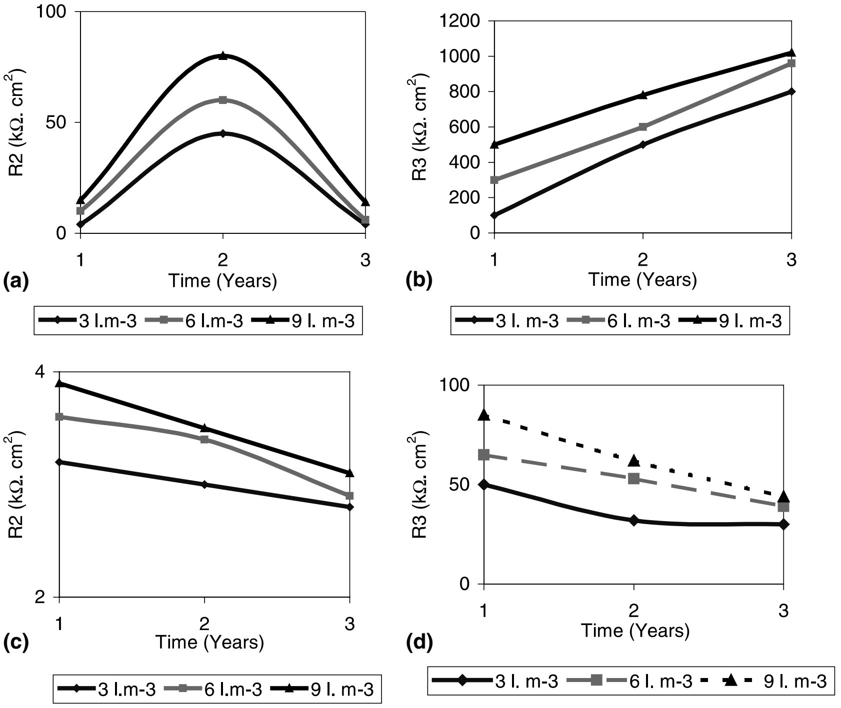

Fig. 19. Evolution of resistances R2 and R3 with time for specimens added with alkanolamine: (a) water (R2); (b) water (R3); (c) chloride solution (R2); (d) chloride solution (R3).

- After 1 year of immersion, calcium nitrate based inhibitor decreases the solubility of some cement components in the vicinity of reinforcing steel. Then the resistivity of concrete cover is increased and the corrosion rate is lowered. When the immersion exceeds 1 year, the effect of this inhibitor vanished, and steel corrosion rate increased in chloride solution.
- Alkanolamine based inhibitor increases the resistivity of concrete cover but it seems to be aged or to flow out of the concrete after a long time immersion. This inhibitor forms an unstable interfacial layer on steel surface which is able to keep the interface under a passive state and consequently the corrosion intensity decreases. However, when concrete is contaminated by chloride, the efficiency of this layer is lowered and corrosion occurs.

Thus, under the conditions of this study, none of the two tested "commercial" inhibitors showed a long-term effectiveness when applied to concrete contaminated with chloride. However, there is no value of inhibitor content needed to achieve effective inhibition of steel bars.

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