Influence of migrating inhibitor concentration on corrosion resistance of steel reinforcement in concrete

Influência da concentração de inibidor migratório na resistência à corrosão do aço no concreto

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ABSTRACT

To increase the service life and durability of reinforced concrete structures, new technologies have been developed, such as cathodic protection, re-alkalinization, chloride extraction, and the use of corrosion inhibitors. This study evaluated the influence of cement type, concrete cover thickness, and the addition of organic migrating corrosion inhibitor (MCI) on the corrosion resistance of the embedded steel in concrete against the induced action of chloride ions. To accomplish this, corrosion tests were carried out using electrode potential techniques simultaneously with acceleration cycles of chloride attack. Four mixtures with two levels of reinforcement cover (25 and 40 mm) were subjected to 30 weekly cycles of chemical attack: a reference mixture (without inhibitor) and three others adopting concentration levels of 0.30%, 0.45%, and 0.60% of MCI in the volume of concrete. The concrete properties (compressive strength, voids, specific gravity, and water absorption by immersion and capillarity) were verified. In the corrosion tests on reinforced concrete with lower cover thickness, the mixture with 0.60% MCI addition showed the best results: corrosion potential values less negative than -200 mV, with less than 10% probability of corrosion.

RESUMO

Para aumentar a vida útil e durabilidade das estruturas de concreto armado foram desenvolvidas novas tecnologias como a proteção católica, re-alcalinização, extração de cloreto, e o uso de inibidores de corrosão. Este estudo avaliou a influência do tipo de cimento, espessura do cobrimento de concreto e adição de inibidor de corrosão orgânico migratório (MCI) na resistência à corrosão do aço embutido no concreto contra a ação induzida de íons cloreto. Para isso, foram realizados ensaios de corrosão utilizando técnicas de potencial de eletrodo simultaneamente com ciclos de aceleração de ataque de cloretos. Quatro misturas com dois níveis de cobertura do aço (25 e 40 mm) foram submetidas a 30 ciclos semanais de ataque químico: uma mistura de referência (sem inibidor) e outras três adotando níveis de concentração de 0,30%, 0,45% e 0,60% de MCI em volume de concreto. As propriedades do concreto (resistência à compressão, índice de vazios, massa específica e absorção de água por imersão e capilaridade) foram verificadas. Nos ensaios de corrosão em concretos armados com menor espessura de cobrimento, a mistura com adição de 0,60% de MCI apresentou os melhores resultados: valores de potencial de corrosão inferiores a -200 mV, com probabilidade de corrosão inferior a 10%.

1. Introduction

Steel corrosion is one of the main forms of deterioration of reinforced concrete structures. Due to their exposure and communication with the environment, over time, with the advancement of this process, the structures become susceptible to their stability decrease and life span reduction [1, 2].

In the United States the total direct economic impact of corrosion costs attributable to concrete structures, concrete highway bridges, parking garages, retaining walls, tunnels, etc., was measured about US$ 480 billion (for the years 2010 and 2011) [3]. An important factor regarding the durability of materials is their relationship closely with sustainability, so that the preservation of natural resources can be made using more durable materials.

According to Figueiredo [4], the corrosion deals with the degradation of materials by the chemical or electrochemical action of the environment into which the structure is located. That is, when the local atmosphere is ranked as aggressive, the reinforcement corrosion becomes especially worrisome, because the conditions are conducive to the ingress of contaminated fluids through the pores of the concrete cover [5].

Overall, according to Sousa [6], the corrosion results in a significant additional cost, either to replace the corroded material or to compensate the indirect losses such as the need for maintenance and production stoppage. In relation to the steel reinforcement of a concrete structure, the corrosion — in addition to deteriorating the mechanical properties — results in the formation of a bulky product (iron oxides and hydroxides); which, by pressing the concrete cover, can cause cracks or even detachment from that layer.

To enhance the durability of concrete structures, new technologies have been developed that are complementary to concrete quality, such as corrosion inhibitors [7-9] which are a good alternative to steel protection against corrosion, presenting low cost and easy application [10, 11]. The study of Wang *et al*. [12] showed that the hybrid uses of hydroxyl carbon nanotubes and polyvinyl alcohol modifiers as additives to improve the corrosion resistance of rebars in concrete.

Currently, at civil construction, one of the classes of inhibitors that stand out are the migrating corrosion inhibitors (MCI). Studies have verified that this type of organic inhibitor (based on amine carboxylate) is effective to retard and inhibit corrosion of steel bar in concrete. MCIs migrate through the concrete pores and provide corrosion protection for the steel reinforcement by forming a passive layer on its surface [13-17]. According Goyal [18] all specimens treated with corrosion inhibitors showed reduced corrosion rate compared to the control specimens. Organo-functional based inhibitors showed most efficient inhibitor efficiency and barrier properties [18].

Some advantages for corrosion inhibitors: convenient application; lower cost; multiple alternatives; inhibitors are available towards different corrosion mechanism. Some disadvantages for corrosion inhibitors: high requirement of penetrability when applied on the hardened concrete surface; dosage is crucial otherwise it will backfire sometimes [19].

The cover depth and crack width are important in the corrosion process of steel in reinforced concrete. Concrete specimens with cover of 45 mm were more effective to slow down the corrosion rate of steel [20].

This research has the concern to extend the life span of the structures located in aggressive environments. For this, besides the quality control of the concrete, it was proposed the use of a migrating corrosion inhibitor as an admixture in the fresh concrete. Therefore, the objective of this experimental study was to assess the development of steel corrosion in concrete against the induced action of chloride ions when this system is under the influence of various MCI concentrations and different reinforcement cover thicknesses.

2. Materials and Methods

2.1. Materials

The materials used in the tests and the preparation of the reinforced concrete specimens were: Portland cement (CPII F 40); river sand and gravel (gneiss) as natural fine aggregate and coarse

aggregate, respectively; water from the public dealership; and CA-50 steel bars with diameter of 10 mm and length of 300 mm. An amine carboxylate based migrating inhibitor was added to the concrete during its production and a salt solution of sodium chloride (NaCl 6%) was employed to accelerate the chemical attack.

2.2. Preparation of steel bars

The preparation of the steel surface was performed by a cleaning procedure that removes the oxides present in the bars, per Practice ASTM G1-03 [21], in both before and after the corrosion tests. The steel bars were immersed in 1:1 hydrochloric acid solution with 3.5 g/L hexamethylenetetramine for ten minutes. After this time, the bars were washed with water in abundance and cleaned with a wire brush (Figure 1a) to extract all the corrosion products.

Then the bars were immersed in acetone, for two minutes, to ensure a quick drying (Figure 1b). After preparation, all bars were individually weighed and then each end coated with electroplater's tape to delimit the area that the aggressive agent will attack (Figure 1c).

Figure 1 - Washing and brushing of steel bars (a), bars immersed in acetone for quick drying (b), and corrosion area delimitation with electroplater's tape (c).

2.3. Prismatic molds manufacturing

The molds for the reinforced concrete specimens were produced with waterproof marine plywood of 10 mm, per Standard Method ASTM G109 [22]. A total of 16 molds for a specimen size of $280 \times 150 \times 115$ mm were produced. To position the bars in the molds as well as to prevent its movement during molding, holes of the same diameter of the bars were drilled on both vertical sides. Before concreting, the molds were lightly greased with a release agent to prevent the adhesion of fresh concrete, thus making the unmolding process easier. Then, the steel bars were placed into the holes intended for them, as parallel to each other as possible.

2.4. Definition of independent variables

To accomplish the aforementioned objectives, the following variables were defined in the experiment: concentration of migrating corrosion inhibitor and concrete cover thickness. The determination of the inhibitor concentration was done by adopting the manufacturer's recommended concentration: 0.60% (in relation to concrete volume) as high level of MCI addition. For the low and medium levels were established concentrations of 0.30% and 0.45%, respectively. These values were not too distant to obtain greater precision in the results, aiming reduce the cost and increase the efficiency of the product.

The concrete cover was evaluated on two levels: 40 mm, according to the environmental aggressiveness Class III, which is rank as strong, adopted in this work and described by the Standard NBR 6118 [23]; and 25 mm, recommended by the Standard ASTM G109 [22] to facilitate the corrosion observation.

2.5. Concrete manufacturing

The concrete mixtures were made in accordance with Standard NBR 5738 [24]. The concrete mixture proportions were performed by using the methodology of the Technological Research Institute of the State of São Paulo (IPT/USP). To evaluate the workability, concretes were characterized by their slump, as Standard NBR 8953 [25], considering conventional launching for structural elements in the order of 100 mm with a variation of $\pm$ 2 mm.

The design compressive strength was established in accordance with Standard NBR 6118 [23], adopting an environmental aggressiveness Class III, considered strong, in marine or industrial environment, and with a big risk of deterioration caused by corrosion. This standard also relates the environmental aggressiveness Class III to a reinforced concrete of Class C30. The standard NBR 8953 [25] ranks this Class C30 concrete to the group of resistance I, defining a design compressive strength of 30 MPa.

Four concrete mixtures were manufactured varying the MCI concentrations (0%, 0.30%, 0.45% and 0.60%). The mixture proportion (by mass) to the reference concrete M1 (without corrosion inhibitor) and to the concrete M2 (with low MCI concentration) was 1 : 1.701 : 2.355 : 0.484 (cement: sand : gravel : w/c ratio).

Concrete mixtures with medium and high MCI concentrations (M3 and M4, respectively) had a small variation in relation to M1 and M2 due to the consistency correction of the concrete mixture, which was influenced by the moisture of the sand, at the manufacturing day. Thus, the mixture proportion (by mass) was 1 : 1.494 : 2.17 : 0.484. The final proportions of the materials to produce 35 liters of concrete, for each mixture, are shown in Table 1.

Table 1 - Materials proportions and mixtures designation.

	Mixture	Cement (Kg)	Sand (Kg)	Gravel (Kg)	Water (Kg)	MCI (ml)
M1	Reference Concrete with CPII F 40	15.33	26.09	36.11	7.42	–
M2	Concrete with CPII F 40 and 0.30% of MCI	15.33	26.09	36.11	7.42	10.50
M3	Concrete with CPII F 40 and 0.45% of MCI	16.36	24.44	35.57	7.92	15.75
M4	Concrete with CPII F 40 and 0.60% of MCI	16.36	24.44	35.57	7.92	21.00

2.6. Properties of concrete

To verify the concrete properties, the following tests were carried out: consistency of fresh concrete by Standard NBR NM 67 [26]; compressive strength by Standard NBR 5739 [27]; water absorption by capillarity as per Standard NBR 9779 [28]; and determination of absorption by immersion, voids, and specific gravity by Standard NBR 9778 [29]. For this, a total of 40 cylindrical specimens 100×200 mm (diameter and height) were produced as recommended by standard NBR 5738 [24], with 10 cylindrical specimens for each mixture: six for the compressive strength test; two for the absorption test by capillarity; and two for the absorption and voids test.

2.7. Corrosion evaluation: electrochemical and non-electrochemical tests

Corrosion tests were performed by means of electrochemical and non-electrochemical methods on prismatic specimens of reinforced concrete, which were made in the laboratory as described in Standard G109 [22]. For this research, a total of 16 prismatic specimens of $280 \times 150 \times 115$ mm were produced, with four specimens for each mixture: two with 25 mm cover thickness; and other two with 40 mm. To perform the tests, it was necessary to couple a plastic dam to the top surface of each prismatic specimen, where a salt solution containing aggressive agent was inserted, as described in Standard ASTM G109 [22].

The electrode potential technique, outlined in Figure 2, was based on the Standard ASTM C876 [30], where the potential difference measurements between the working electrode (reinforcement) and a reference electrode (for this work a copper sulfate electrode) are carry out with the help of a high impedance voltmeter. The technique presents a standard procedure for the evaluation of corrosion phenomenon, as in Table 2, through a correlation between potential intervals and the probability of its occurrence.

To accelerate the corrosion process, the specimens were submitted to semi cycles of drying and of exposure to salt solution in accordance with Test Method ASTM G109 [22]. The volume of this solution was 400 ml of sodium chloride (NaCl 6%). The specimens were exposed to chloride ions attack for 3 days. Then, the solution was drained from dam, and the potential measurements were made. Thereafter, the drying procedure was carried out for 4 days. This cycle was repeated for 30 weeks.
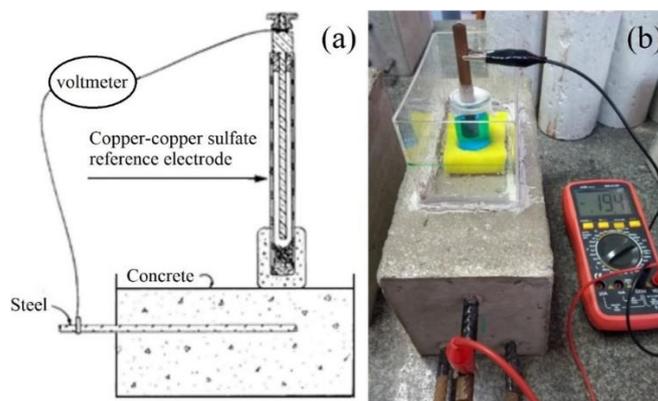
Figure 2 - Detailed scheme for electrode potential measurements (a) and system assembly in the laboratory (b). Adapted from Test Method ASTM C876 [30].

Table 2 - Evaluation of corrosion potential. Adapted from Test Method ASTM C876 [30].

Potential (mV)	Corrosion Probability	Analysis
More positive than -200mV	< 10%	No corrosion
Between -200mV and -350mV	Uncertain	Evidence of corrosion
More negative than -350mV	> 90%	Active corrosion

A copper-copper sulfate reference electrode (Figure 3a) was produced to perform the corrosion potential tests as described in Test Method ASTM C876 [30]. For this, the necessary materials were: a) solid copper rod of diameter and length greater than or equal to 6 mm and 50 mm, respectively; b) saturated solution of copper sulfate; c) a glass tube with an internal diameter greater than or equal to 25 mm with a glass plate, or a thin porous plug attached to one end; d) plastic paraffin film with paper to seal the top of glass tube; and e) simple sponge, used as electrical junction device, pre-wetted with a low electrical resistance contact solution (neutral household detergent diluted with potable water).

The reference electrode assembly was accomplished by filling three quarters (3/4) of the glass tube with the saturated solution of copper sulfate and by placing the copper rod inside the tube without touching the sides or bottom. To seal the electrode as well as to fix the rod, the plastic paraffin film was applied at the top of tube. Moreover, at the bottom, it was placed the sponge pre-wetted with dilute detergent, as shown in Figure 3b. This saturated sponge provides a low electrical resistance liquid bridge between the surface of the concrete and the reference electrode.

After the end of the cycles of chemical attack and potential measurements, the prismatic specimens were broken in a hydraulic press for the compressive strengths evaluations and the upper steel bars were removed for the determination of gravimetric corrosion rate and for the visual analysis with an optical microscope. The bars were cleaned by the same procedure that was used on specimens' preparation, with the care to remove only corrosion products without significant removal of base steel, ensuring an accurate determination of the mass loss, as described in Practice ASTM G103 [22]. With a microscopic examination (with 6.3× zoom), the adequate removal was confirmed. This examination also revealed the extent of corrosion damage, observing the effects of the corrosion penetration caused by pitting-type corrosion.
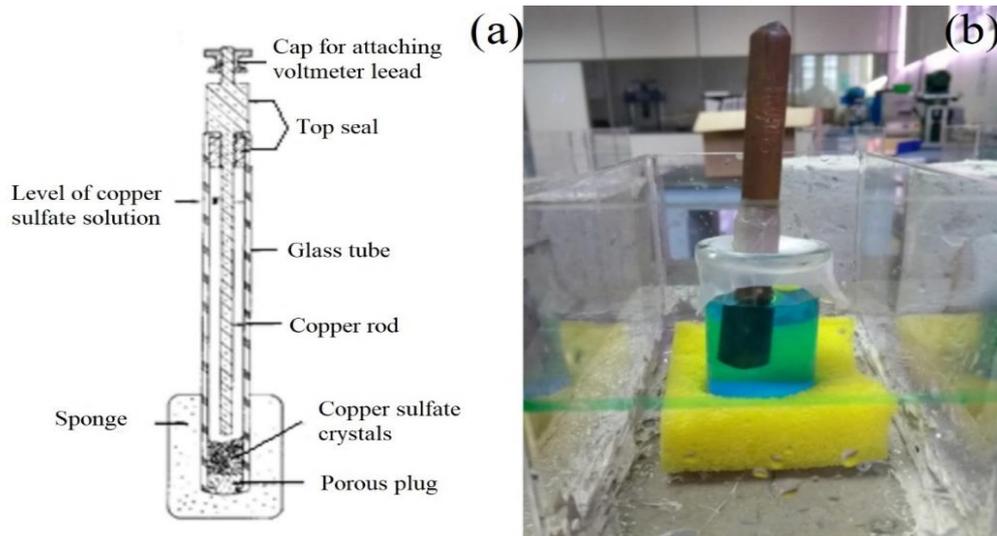
Figure 3 - Detailed scheme of the copper-copper sulfate reference electrode. Adapted from Test

Method ASTM C876 [30] (a) and electrode assembly in the laboratory (b).

After cleaning, the steel bars were again weighed to determine their mass loss during the corrosion test period. According to Ribeiro [31] and the Practice ASTM G1-03 [22], the gravimetric corrosion rate (CR) may be obtained as follows:

$$CR = (K \times W)/(A \times T \times D) \qquad (1)$$

where:

K = a constant, for millimeters per year (mm/y) as CR unit desired, K = 8.76×10^4;

W = mass loss in grams (g);

A = area (cm²), for this study 20 cm²;

T = time of exposure in hours (h), for this study 5,040 hours (210 days); and

D = density in g/cm³, for CA-50 Steel, D = 7.85 g/cm³.

The Standard Practice NACE SP0775 [32] ranks the uniform corrosion rate, according to its corrosivity, as shown in Table 3.

Table 3 - Corrosivity classification. NACE SP0775 [32].

Uniform corrosion rate (mm/y)	Pitting corrosion rate (mm/y)	Corrosivity
< 0.025	< 0.13	Low
0.025 – 0.12	0.13 – 0.20	Moderate
0.13 – 0.25	0.21 – 0.38	High
> 0.25	> 0.38	Severe

To estimate the corrosion inhibition efficiency of steel in concrete specimens with various MCI concentrations, a method adapted by Bolina [33] was used. The percentage of efficiency, Ef, of each situation was estimated based on the values of gravimetric corrosion rate (system corrosion rate without inhibitor, Ts, and with inhibitor, Tc), obtained by mass loss of the steel bars, during the period of corrosion tests. The following relation was used:

$$Ef = [(Ts - Tc)/(Ts)] \times 100 \qquad (2)$$

3. Results

3.1. Examination of the concrete properties

3.1.1. Compressive strength

Figure 4 shows the compressive strength values found for each specimen as well as its average and standard deviation. It can be observed that all the mixtures reached values greater than the design compressive strength of 30 MPa. Mixtures with different inhibitor contents presented very close average values of compressive strength when compared to the reference concrete.
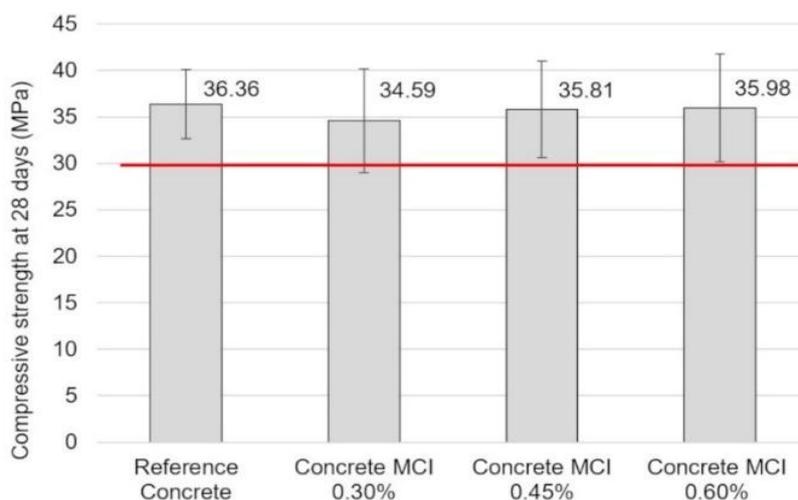
Figure 4 - Average compressive strength of mixtures at 28 days.

3.1.2. Absorption, voids and specific gravity

By comparing the results for each mixture from Table 4, the concrete with 0.60% MCI stood out, because it presented the lower average values of absorption by immersion, 5.551%, and of voids, 12.594%, what avoided the chloride ions penetration; since these factors are directly related to the transport rate of aggressive agents into the concrete. According to Silva [34], the amine-based corrosion inhibitor can absorb part of the mixture's water or react in some way with the silicates present in the cement paste, reducing the absorption and voids.

The physical properties of the other concretes with MCI, in lower concentrations, presented worse results than the reference concrete. The concrete with 0.30% MCI obtained the highest values of absorption and voids, 6.560% and 14.609%, respectively, and the smallest value of average compressive strength, 34.59 ± 5.59 MPa. Therefore, there is the need for the correct dosage of the inhibitor to maintain or even improve these physical properties.

The specific gravities showed very small variations with the addition of different inhibitor concentrations. However, in general, it can be stated that the addition of 0.60% of MCI provided a higher density of concrete due to a higher dry specific gravity (2.272 g/cm³) and smaller specific gravity (2.600 g/cm³).

Table 4 - Average values of water absorption by immersion, voids, and specific gravity.

	Mixture	Absorption by immersion (%)	Voids (%)	Specific gravity (g/cm³)	Saturated specific gravity (g/cm³)	Dry specific gravity (g/cm³)
M1	Reference Concrete	6.059	13.692	2.618	2.397	2.260
M2	Concrete with MCI 0.30%	6.560	14.609	2.608	2.373	2.227
M3	Concrete with MCI 0.45%	6.167	13.836	2.604	2.382	2.244
M4	Concrete with MCI 0.60%	5.551	12.594	2.600	2.398	2.272

The data given in Table 5 shows the average capillary absorption was smaller for the 0.60% MCI-treated concrete throughout the test time. For Helene [35], this occurs when the concrete capillaries have smaller diameters and are less intercommunicable. This result was also confirmed by the smaller value of average voids obtained for this mixture. The highest capillarity coefficients were observed for concrete with 0.30% MCI.

Table 5 - Average values of water absorption by capillarity.

| Mixture | | Absorption by capillarity (g/cm^2) | | | | |
| | | Time (hours) | | | | |
		3 h	6 h	24 h	48 h	72 h
M1	Reference Concrete	0.461	0.588	1.052	1.263	1.398
M2	Concrete with MCI 0.30%	0.484	0.629	1.126	1.364	1.520
M3	Concrete with MCI 0.45%	0.450	0.597	1.053	1.282	1.423
M4	Concrete with MCI 0.60%	0.438	0.569	1.022	1.252	1.389

3.2. Evaluation of steel corrosion

3.2.1. Corrosion potential measurements

In the graphical representation of the corrosion potential measurements, for the tested specimens, the electrode potential (mV) was graphed as a function of the chemical attack induction cycles (weeks), considering the four concrete mixtures (M1, M2, M3, and M4) and the two thicknesses of concrete cover, 25 mm and 40 mm, as shown in Figures 5 and 6.

From the graph in Figure 5, plotted for a 25 mm concrete cover, it was possible to verify that the potential readings of the test specimens M1, M2 and M3 reached values more negative than -350 mV, according to the progress of the cycles. Which indicate a probability greater than 90% of corrosion occurrence, that is, in these mixtures occurred the depassivation of the reinforcement and the onset of the corrosion, ASTM C876 [30]. The M4 mixture with 0.60% MCI addition, concentration indicated by the manufacturer, showed no signs of corrosion and its potential measurements were more positive than -200 mV; remaining in the range of less than 10% probability of steel corrosion throughout the test period.
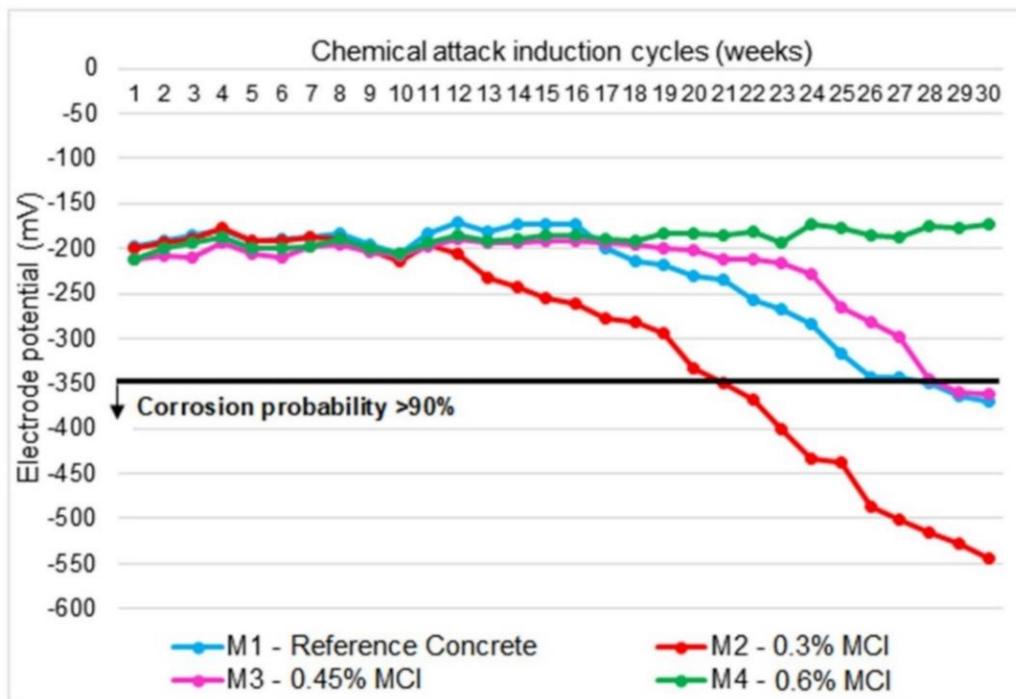
Figure 5 - Average electrode potential readings for 25 mm of concrete cover.

Analyzing the three mixtures that developed corrosion, it can be reported that the mixture M2 was the first one to present the depassivation of the reinforcement and the onset of the corrosive process, in the 21st week of cycles. Thus, there is an inhibition inefficiency of the 0.30% MCI concentration that was added to concrete. The M1 and M3 mixtures crossed the threshold of -350 mV a little later, in the 28th week of cycles; indicating a greater capacity of preservation of the potentials, but not totally effective.

In the graph of Figure 6, the electrode potential measurement curves were drawn for the same mixtures, but with 40 mm concrete cover. In this chart, the mixtures M3 and M4 presented potential measures corresponding to an area of less probability of corrosion, where the values are more positive than -200 mV, ASTM C876 [30]. By increasing the cycles of induction of chemical attack, M1 and M2 tended to make results in the range of -200 to -350 mV, where the corrosion activity of the reinforcing steel is uncertain. Thus, with the prolongation of the period of testing, it would be possible to better visualize the corrosion development in the specimens with greater thickness of concrete cover.

Due to this higher concrete cover, the results in Figure 6 were less negative than those in Figure 5. The concrete cover over the reinforcement provides a physical protection to the steel, making difficult the ingress of aggressive ions of the environment, like the chlorides [35-37]. Therefore, in addition to the protection provided by the inhibitor, the depth of 40 mm concrete cover also acted to improve the corrosion resistance of the steel in relation to mixtures with 25 mm concrete cover.

3.2.2. Gravimetric corrosion rate

The graphs of Figures 7a–b allows a clearer view of the relationship between the average corrosion rate at the end of the cycles and the inhibitor content added to the mixtures. In both graphs, the curves show the highest corrosion peak for the mixture with 0.30% MCI addition and the lowest for the 0.60% MCI mixture. The concretes of reference and with 0.45% MCI addition had close values; nevertheless, the M3 concretes outcomes were better.
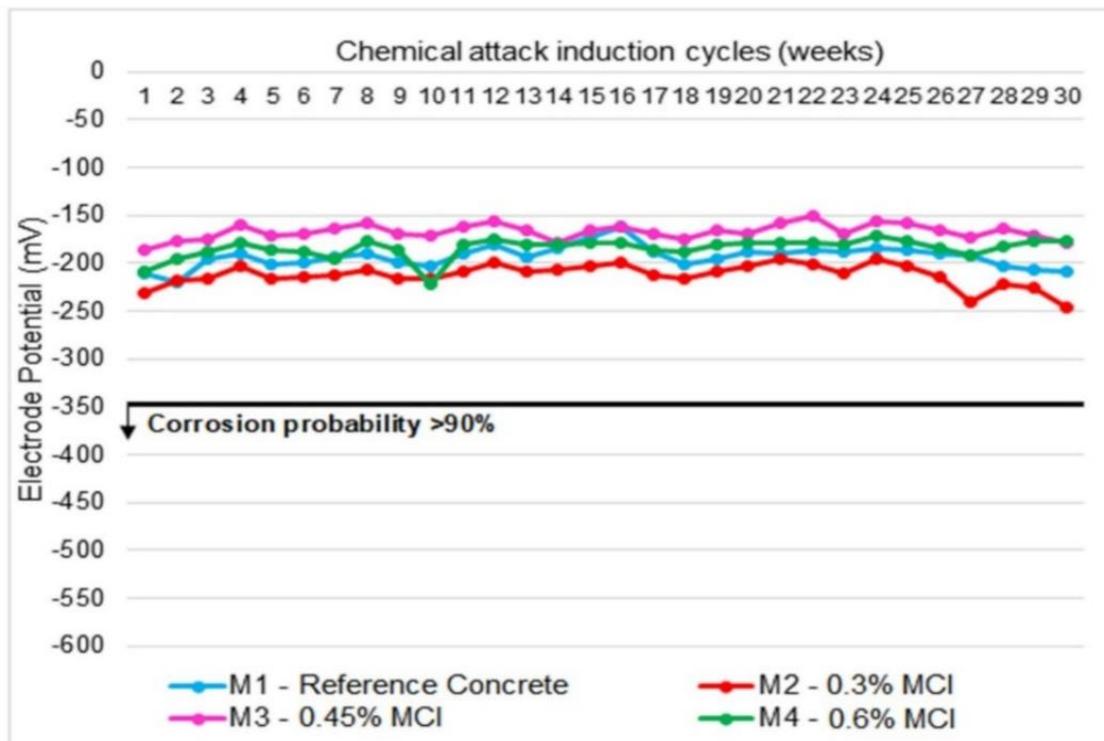
Figure 6 - Average electrode potential readings for 40 mm of concrete cover.

The concrete cover represents the main factor for the distinction of the graphs. The corrosion rate values of first one, Figure 7a, were higher when compared to the values in the

second graph, Figure 7b; considering all mixtures. It is noticeable that concrete cover thickness exerted a critical influence on corrosion inhibition, since the thicker cover provided better protection against the corrosive process. For this study, the MCI was incorporated into fresh concrete as an admixture rather than applied on hardened concrete as a surface treatment.
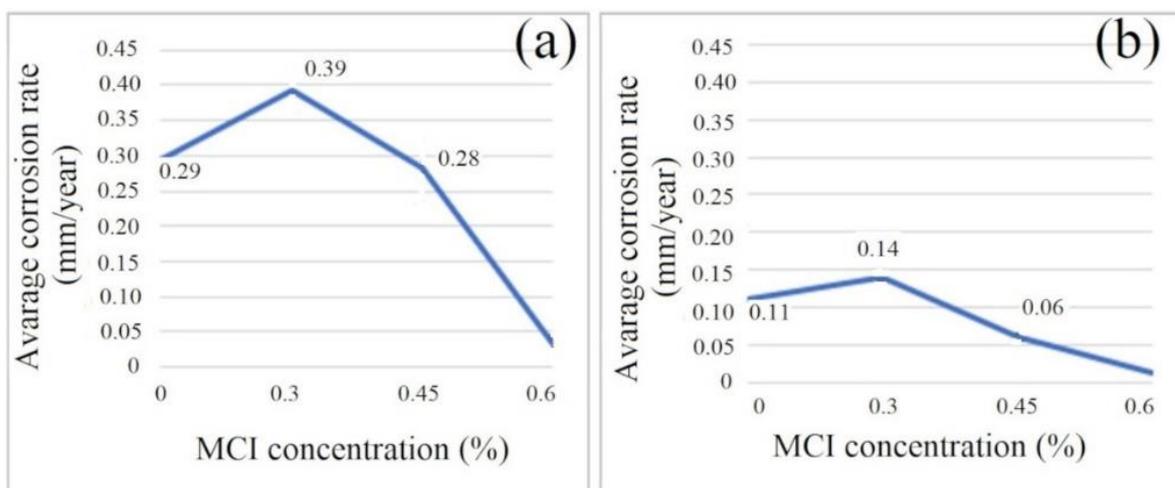
Figure 7 - Average corrosion rate versus MCI concentration, for concrete cover of 25 mm (a) and 40 mm (b).

3.2.3. Inhibition efficiency

Table 6 shows the values of corrosion protection efficiency of steel for the MCI treated specimens, which were attacked by chlorides; considering the results obtained using the corrosion rate technique. From this Table, the dosage with the highest inhibition efficiency was that with 0.60% MCI concentration, with percentage values of 88.68% and 90% for 25 mm and 40 mm concrete cover respectively. The 0.45% MCI content had a low performance in corrosion protection of steel, with an average efficiency of 45% for the thicker cover. For the less thick (25 mm), the result was almost nil. The 0.30% MCI addition did not achieve any inhibition efficiency, as already noticed herein in the other tests.

Nóbrega [38] and Silva [34] explain that corrosion inhibitors for concrete have an optimal point of addition and that, for values above or below this concentration, they may have an inverse behavior: that is, acceleration of the corrosive process instead of mitigation. Their results about corrosion show the importance of the careful analysis in the specification of this type of chemical admixture.

Table 6 - Inhibition efficiency for various MCI concentrations.

MCI content (%)	Concrete Cover (mm)	Inhibition Efficiency (%)
0.30	25	0.00
	40	0.00
0.45	25	3.77
	40	45.00
0.60	25	88.68
	40	90.00

3.2.4. Visual inspection of the steel bars

All top bars of the specimens were examined, in which measurements of the electrode potential and the gravimetric corrosion rate were also carried out. According to Cascudo [36], a variety of corrosion products can be found in CA-50 steel when the attack occurs by chlorides, such as: Lepidocrocite (γ-Fe(OH)), Akaganeite (β-FeO(OH)), Goethite (α-FeO(OH)), Maghemite (γ-Fe$_2$O$_3$) and Erithrossiderite (K$_2$FeCl$_5$.H$_2$O).

In this visual inspection, characteristic aspects of corrosion were identified in the steel bars that presented the highest corrosion rates, that is, a severe or high corrosion. In Figures 8 to 11, an optical microscope was used to examine, in detail, the corrosion products of these bars.

Figure 8 exhibits the top bar examination of replicate 2 of M1, for 25 mm concrete cover. Its corrosion rate and the last measurement of the electrode potential were 0.343 mm/year and -440 mV respectively.

As depicted in Figure 8a, it was possible to identify several localized corrosions, confirming the results previously obtained. At points 1, 2 and 3 (with 6.3× zoom, see Figure 8b), it can be observed the corrosion pits that, according to Silveira *et al.* [40], are usually cavities of small opening and greater depth, with little or no uniform loss; therefore, very destructive and dangerous.

According to the authors, the general cause of pitting corrosion of metals is the existence of small areas highly anodic in relation to adjacent cathodic areas, what create a local corrosion cell; the so-called "batteries" of corrosion. At point 4, there is a yellowish spot of rust, that is, the formation of the basic products of corrosion: $FeO_3.nH_2O$ and $Fe(OH)_3.FeCl_3$ [1].
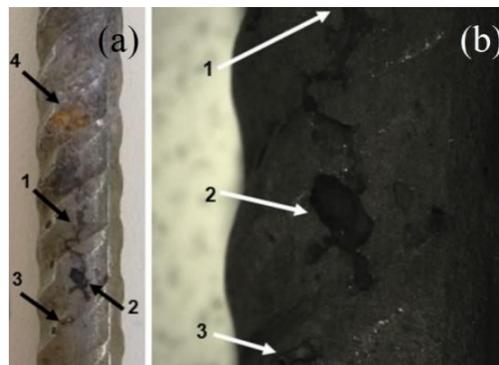
Figure 8 - Aspect of the embedded top bar of replicate 2 of M1, without MCI and with 25 mm concrete cover. No zoom (a); and with 6.3× zoom (b).

Figures 9a and 10a detail the embedded bars of the M2 mixtures (replicates 1 and 2 respectively), for 25 mm concrete cover. Black corrosion products were identified in these bars, which can be a sign of formation of magnetite (Fe_3O_4), according to Bolina [33]. Other reddish orange corrosion products also appear in the dark substrate. In addition, an irregular surface with crusts of corrosion products can be noticed in these Figures.

The corrosion rates and corrosion potential values of these steel bars indicate this deterioration: for the first replicate, 0.421 mm/year and -551 mV respectively; and for the second replicate, a slightly lower rate of 0.365 mm/year and potential of -538 mV. The Points 1 and 2, highlighted in Figure 9a (with 6.3× zoom, see Figure 9b), were cases of pitting corrosion; and at points 1, 2 and 3, in Figures 10a–b, irregularities and cross-section losses have occurred.
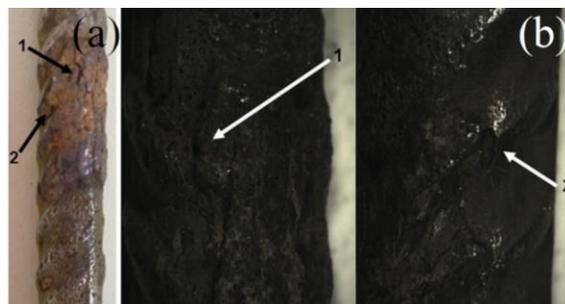
Figure 9 - Aspect of the embedded top bar of replicate 1 of M2, with 0.30% MCI and 25 mm concrete cover. No zoom (a) and with 6.3× zoom (b).
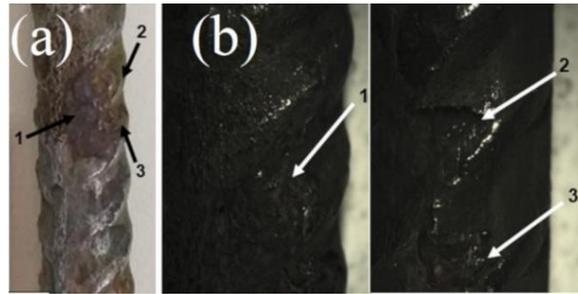
Figure 10 - Aspect of the embedded top bar of replicate 2 of M2, with 0.30% MCI and 25 mm concrete cover. No zoom (a) and with 6.3× zoom (b).

Concerning the system with 0.45% MCI addition, M3 mixtures, the corrosion of the steel bars presented softer aspects; and only in the replicate 1 with a 25mm concrete cover (see Figure 11a). Point 1 indicates a pitting corrosion, and point 2 shows both yellowish corrosion products and irregularities on the steel surface (see Figure 11b). The visual aspect was very pronounced and complied with the performance of the inhibitor used. The results of corrosion potential and electrochemical corrosion rates were -378 mV and 0.332 mm/year respectively.

With the aid of the X-ray photoelectron spectroscopy (XPS) method, Bavarian and Reiner [39] carried out a chemical analysis of the concrete reinforcement in the presence of an MCI based on amino-carboxylate chemistry. They verified nitrogen peaks on the surface of the steel bars treated with MCI, which did not occur in the untreated bars.

These amine-rich compounds on the steel bars surface were associated with the amine-based inhibitor. Chemical quantification also revealed organic compounds with carboxylate chemistry in these bars. The results showed that both MCI and aggressive agents (chlorides) had migrated in through the concrete pores and had reached the reinforcement, but MCI had formed a protective layer on the steel surface, protecting the rebar. The conclusions were promising in both this study and that of Bavarian *et al*. [13], because the MCI demonstrated a great efficiency in the protection for steel in aggressive environments.
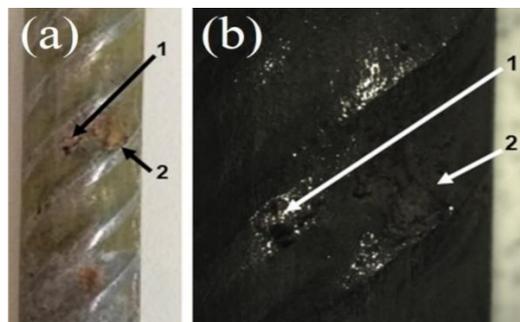
Figure 11 - Aspect of the embedded top bar of replicate 1 of M3, with 0.45% MCI and 25 mm concrete cover. No zoom (a) and with 6.3× zoom (b).

4. Conclusion

Amine-based inhibitor addition proved to be an efficient method for corrosion inhibition of steel in reinforced concrete. It was verified that not all MCI concentrations generated a corrosion protection system, with only the mixture M4 (with 0.60% MCI) demonstrating inhibitory efficiency.

Regarding to physical and mechanical properties of the concretes, the mixture with 0.60% of MCI presented lower values of absorption by immersion and voids (5.55% and 12.59% respectively), as well as lower absorption by capillarity. The reference concrete had the highest average compressive strength (36.36 MPa ± 3.74) followed by the M4 concrete (35.98 ± 5.81 MPa).

The electrode potential test allowed the identification of the mixtures and cover thicknesses that performed better in terms of corrosion resistance of the steel. The 0.60% MCI-

treated mixture showed the less negative potential values, remaining in the range where there is less than 10% probability of corrosion throughout the test period.

The M2 mixture (with 0.30% MCI) had the worst performance among all of them, with reinforcement depassivation and the onset of the corrosive process occurring in the 21st week of the cycle. The other mixtures (M1 - reference concrete and M3 - 0.45% MCI) also reached the range where the corrosion probability is greater than 90% but did so later (28th week).

The concrete cover over the reinforcement influenced the corrosion resistance of the steel, providing a physical protection and making it difficult for chloride ions to ingress. The mixtures with a 25 mm cover presented more negative potential values than the mixtures with a 40 mm cover.

The values of the gravimetric corrosion rates (CR) of the steel bars were consistent with the results of the electrode potential readings. The steel bars of M4 mixture had the lowest corrosion rates. This experiment confirmed the higher susceptibility to corrosion of the steel from the M2 mixture (with 0.30% MCI and 25 mm cover), showing severe corrosivity (0.421 mm/year).

M1 and M3 concrete mixtures also showed high corrosivity, reaching values of 0.343 mm/year and 0.332 mm/year respectively. The visual inspection allowed the characterization of some common aspects of the corrosive process in the steel bars that showed higher corrosion rates, such as yellowish and dark spots, pitting and fissures.

According to the results obtained by this research, the appropriate use of corrosion inhibitors (at the optimal point of addition) was demonstrated to be an important tool regarding the prevention or control of the corrosive process. This treatment with MCI admixtures can reduce the need for maintenance as well as increase the lifespan of reinforced concrete structures. However, these inhibitors do not have the function of avoiding the occurrence of corrosion in its entirety, since they are complementary to good construction technique.

References

[1] V. Gentil, *Corrosion*, 5 ed., LTC, 345pp., Rio de Janeiro, Brazil (2007).

[2] M. Carsana, F. Canonico, L. Bertolini, Corrosion resistance of steel embedded in sulfoaluminate-based binders, *Cement and Concrete Composites*, 88, 211-219 (2018). https://doi.org/10.1016/j.cemconcomp.2018.01.014.

[3] U. M. Angst, Challenges and opportunities in corrosion of steel in concrete. Mater Struct 51, 4 (2018). https://doi.org/10.1617/s11527-017-1131-6.

[4] E.P. Figueiredo, *Corrosion and degradation of materials. In: Building Materials and Principles of Materials Science and Engineering*, Isaia GC (Editor), IBRACON, V1, pp. 377-402, São Paulo, Brazil (2007).

[5] L. Bertolini, *Building materials: pathology, rehabilitation and prevention*, Text workshop, pp. 414, São Paulo, Brazil (2010).

[6] C.A.C. de Sousa, *Principles of electrochemical corrosion, In: Ribeiro DV. Corrosion in reinforced concrete structures*, 7 ed., Elsevier, pp. 13-35, Rio de Janeiro, Brazil (2014).

[7] N. Gartner, T. Kosec, A. Legat, The efficiency of a corrosion inhibitor on steel in a simulated concrete environment, *Materials Chemistry and Physics*, 184, 31-40 (2016). https://doi.org/10.1016/j.matchemphys.2016.08.047.

[8] R. Vedalakshmi, K. Rajagopaland, N. Palaniswamy, Determination of migration efficiency of amino alcohol based migrating corrosion inhibitor through concrete, *Corrosion Engineering, Science and Technology*, 44(1), 20-31 (2009). https://doi.org/10.1179/174327808x272405.

[9] L. Z. Yong, Z. X. Gang, L. X. Lin, Effect of migrating corrosion inhibitor on corrosion rate of reinforcing steel in concrete with various admixed chloride, *Applied Mechanics and Materials,* 204, 3146-3150 (2012). https://doi.org/10.4028/www.scientific.net/AMM.204-208.3146.

[10] T. A. Söylev, M. G. Richardson, Corrosion inhibitors for steel in concrete: State-of-the-art report, *Construction and Building Materials,* 22(4), 609-622 (2008). https://doi.org/10.1016/j.conbuildmat.2006.10.013.

[11] J. S. Cai, C. C. Chen, J. Z. Liu, L. Shi, The protection of reinforcing steel in concrete by migrating corrosion inhibitor, *Key Engineering Materials*, 629, 630, 136-143 (2015). https://doi.org/10.4028/www.scientific.net/KEM.629-630.136.

[12] Z. Wang, J. Yu, G. Li, M. Zhang, C. K. Leung, Corrosion behavior of steel rebar embedded in hybrid CNTs-OH/polyvinyl alcohol modified concrete under accelerated chloride attack, *Cement and Concrete Composites*, 100, 120-129 (2019). https://doi.org/10.1016/j.cemconcomp.2019.02.013.

[13] B. Bavarian, A. O. Alaba, L. Reiner, J. Meyer, *Migrating Corrosion Inhibitors to Protect Steel Reinforced Concrete Structures, Materials performance*, pp. 20–23, St. Paul, Minnesota, USA (2018).

[14] R. Myrdal, *Corrosion Inhibitors – State of the art*. In: COIN Project Report 22 - 2010, Oslo, SINTEF Building and Infrastructure (2010).

[15] M. Z. Lourenço, C. A. C. de Souza, *Protective methods and increased durability of reinforced concrete, In: Corrosion in reinforced concrete structures* (ed. by Ribeiro DV), 7 ed., pp. 119-170. Elsevier, Rio de Janeiro, Brazil (2014).

[16] T. Chaussadent, V. Nobel-Pujol, F. Farcas, I. Mabille, C. Fiaud, Effectiveness conditions of sodium monofluorophosphate as a corrosion inhibitor for concrete reinforcements, *Cement and Concrete Research*, 36, 556-561 (2006). https://doi.org/10.1016/j.cemconres.2005.09.006.

[17] F. Bolzoni, A. Brenna, G. Fumagalli, S. Goidanich, L. Lazzari, M. Ormellese, M. P. Pedeferri, Experiences on corrosion inhibitors for reinforced concrete, *International Journal of Corrosion and Scale Inhibition*, 3(4), 254-278 (2014). https://doi.org /10.17675/2305-6894-2014-3-4-254-278.

[18] A. Goyal, E. Ganjian, H. S. Pouya, M. Tyrer, Inhibitor efficiency of migratory corrosion inhibitors to reduce corrosion in reinforced concrete exposed to high chloride environment." Construction and Building Materials 303 (2021): 124461. https://doi.org/10.1016/j.conbuildmat.2021.124461

[19] J. Y. Hu, S. S. Zhang, E. Chen, W. G. Li, A review on corrosion detection and protection of existing reinforced concrete (RC) structures. Construction and Building Materials 325 (2022): 126718. https://doi.org/10.1016/j.conbuildmat.2022.126718.

[20] H. Z. Lopez-Calvo, P. Montes-García, V. G. Jiménez-Quero, H. Gómez-Barranco, T. W. Bremner, M. D. A. Thomas, Influence of crack width, cover depth and concrete quality on corrosion of steel in HPC containing corrosion inhibiting admixtures and fly ash, *Cement and Concrete Composites*, 88, 200-210 (2018). https://doi.org/10.1016/j.cemconcomp.2018.01.016

[21] ASTM - American Society for Testing and Materials, G1-03: Standard Pratice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, United States (2017).

[22] ASTM - American Society for Testing and Materials G109: Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments, United States (2013).

[23] ABNT, Brazilian Association of Technical Standards, NBR 6118: Design of concrete structures – Procedure, Rio de Janeiro (2014).

[24] ABNT, Brazilian Association of Technical Standards, NBR 5738: Concrete - Procedure for molding and curing concrete test specimens. Rio de Janeiro (2016).

[25] ABNT, Brazilian Association of Technical Standards, NBR 8953: Concrete for structural use - Density, strength and consistence classification, Rio de Janeiro (2015).

[26] ABNT, Brazilian Association of Technical Standards, NBR NM 67: Concrete - Slump test for determination of the consistency, Rio de Janeiro (1998).

[27] ABNT, Brazilian Association of Technical Standards, NBR 5739: Concrete - Compression test of cylindrical specimens, Rio de Janeiro (2018).

[28] ABNT, Brazilian Association of Technical Standards, NBR 9779: Mortar and hardened concrete - Determination of water absorption by capillarity, Rio de Janeiro (2012).

[29] ABNT, Brazilian Association of Technical Standards, NBR 9778: Hardened mortar and concrete - Determination of absorption, voids and specific gravity, Rio de Janeiro (2009).

[30] ASTM - American Society for Testing and Materials, C876: Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete, United States (2015).

[31] D. V. Ribeiro, Influence of the addition of red mud on the properties and corrosivity of reinforced concrete, *Dissertation* (Doctorate in Materials Science and Engineering), Federal University of São Carlos, São Paulo, Brazil (2010).

[32] NACE - National Association of Corrosion Engineers, Standard SP0775, Preparation, Installation, Analysis and Interpretation of Corrosion Coupons in Oilfield Operations (2018).

[33] C. C. Bolina, Corrosion inhibitors: Performance evaluation against steel corrosion induced by carbonation and chlorides, *These* (Master in Civil Engineering) - Federal University of Goiás, Goiânia, Brazil (2008).

[34] D. R. da Silva, Study of corrosion inhibitors in reinforced concrete, aiming to improve its durability, *Dissertation* (Doctorate in Materials Science and Engineering) - Federal University of Rio Grande do Norte, Natal, Brazil (2006).

[35] P. Helene, Contribution to the study of steel corrosion in reinforced concrete, *Dissertation* (Free Teaching) - Polytechnic School, University of São Paulo, São Paulo, Brazil (1993).

[36] O. Cascudo, *Corrosion Control of Concrete Reinforcement: Inspection and Electrochemical Techniques*, PINI, pp. 233, São Paulo, Brazil (1997).

[37] A. M. Neville, *Properties of concrete*, 5. ed., Bookman, 888 pp., Porto Alegre, Brazil (2016).

[38] A. C. V. Nóbrega, Study of recommended corrosion inhibitors for concrete, *Thesis* (Master in Chemistry), Federal University of Rio Grande do Norte, Center for Exact and Earth Sciences, Natal, Brazil (2004).

[39] B. Bavarian, L. Reiner, "19 - Corrosion protection of steel rebar in concrete using migrating corrosion inhibitors," Editor(s): M. Raupach, In European Federation of Corrosion (EFC) Series, Corrosion of Reinforcement in Concrete, Woodhead Publishing, (2007) 239-249. https://doi.org/10.1533/9781845692285.239.

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