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Evaluation of Corrosion Potentials in Polymeric Mortar Specimens Submitted to Drying and Wetting Cycles in NaCL Solution

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Abstract: Electrochemical methods for the accelerated induction of corrosion in concrete reinforcement are considered to have similar sensitivity to gravimetric methods and to provide quick answers to the research. With a corrosion analyzer instrument and a copper/copper sulphate semicell, the corrosion potentials of the steel inserted in polymeric mortar specimens can be monitored. In this research, CA 60 steel bars were used without protection, with cathodic protection by zinc and with anodic protection by nitrite for 12 drying cycles in autoclave and wetting in NaCl solution. The polymeric mortar (denser, less voids and les water absorption) provides greater protection for steel than 24 MPa concrete (344 kg/m^3 consumption) and the efficiency of protective paints with nitrite-based had comproved.

Key words: electrochemical methods, accelerated induction of corrosion, corrosion potentials, polymeric mortar.

1. Introduction

In the reinforced concrete structures of buildings and art works built in coastal areas that are subjected to the supply of saline mists carried by the wind, chlorides cause many losses due to the need for cost repairs and high risks. Therefore, it is important to research the efficiency of the materials used in structural recoveries, such as polymeric mortar and corrosion inhibitors based on zinc and nitrites in repairs due to corrosion of the reinforcement. The loss of the natural protection of the reinforcement by the concrete covering can occur through several mechanisms, being predominant the depassivation by carbonation and by the action of chlorine ions [1].

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Electrochemical corrosion is actually a network of galvanic batteries in a short circuit placed on the metal surface [2] that requires the existence of a conductor, electrolyte, difference in electrical potential and oxygen to start and maintain the corrosive process [3]. Inside the concrete, the steel is initially protected by the oxide formed on its surface by the combination with the cement alkalis, but it can be altered by the carbonation of the concrete and by the attack of chlorides and sulfates.

Concrete has the ability to protect reinforcement against corrosion, which is mainly due to the electrochemical passivation of reinforcement in the alkaline solution present in the pores of concrete. "Corrosion starts when passivity is broken, partially or completely, either due to carbonation or the presence of chlorides" [4].

This process of corrosion of steel in concrete has an initial phase, in which aggressive agents modify the conditions of the concrete around the bar, breaking the passivating layer and thereby allowing the formation of a corrosion cell, responsible for the spread of corrosion, however, chlorides are the most destructive because of their abundance in coastal areas where many building structures are located and because they are not consumed in the redox reactions [5].

In reinforced concrete structures, to avoid the corrosive process, of course, you cannot remove the steel bars that are the electrical conductors, and the electrolyte formed by the calcium hydroxide of the concrete.. It remains, therefore, to try to eliminate the potential difference in steel bars with zinc-based inhibitors, which act on the anodic zone or on the basis of nitrites that act in the cathodic zone, or to prevent the entry of oxygen by creating a thick layer of micro concrete, like the polymeric mortar used in structural repairs.

2. Objective

This article aims to compare the differences between the protective capacity of the polymeric mortar used in structural repairs with concrete with Fck 24 MPa, and steel bars without protection, with zinc-based and nitrite-based paint protection.

3. Material and Methods

Corrosion inhibitors can decrease the corrosion rate without changing the concentration of corrosive agents [6]. The most used are nitrites (inorganic), amines and alcohol-amines (organic) added to concrete that act as anodic, cathodic or mixed inhibitors that act by absorption, film formation or armature passivation and that, in existing structures, the inhibitors can be used in repair mortars, applied to the concrete surface or holes [7].

There are also organic-based anodic migratory corrosion inhibitors applied to the concrete surface that, if applied as paint, migrate as steam through the pores of the concrete and adhere to the steel by ionic attraction, forming monomolecular film [8].

However, in building structures, when cracks occur in the covering layer or when part of the armature is exposed and requires repairs, anodic and cathodic inhibitors in the form of paint applied to the armature have been widely used due to the ease of acquisition, application and low cost.

Therefore, the importance of research on the effectiveness of structural repairs and, for this, non-destructive tests can be used, such as the measurement of the resistivity of the material and the diffusion of chlorides to characterize the properties of materials and the measurement of corrosion potentials establish its suitability for armor protection.

Resistivity can be used to estimate the probability of corrosion. According to the European Comitee du Beton [9] for Portland cement at 20°C, the conditions expressed in Table 1 occur.

The ultrasonic pulse speed technique, allows to obtain information about the modulus of elasticity and the resistance to compression, being able to identify voids inside the material [10]. Ultrasound is a wave that exceeds 20 KHz and creates a disturbance in the environment in which it spreads, causing the molecules and atoms to vibrate [11]. In this way, the pulse speed is related to the quality of the concrete and according to the English standard BS EM 1254-4/04 [12], the following conditions are admissible (Table 2).

Table 1 Resistivity versus corrosion risk. Source: CEB 192/88.

Resistivity (kΩcm)	Corrosion probability
< 100	Negligible risk
50 to 100	Low risk
10 to 50	Moderate risk
< 10	High risk

Table 2 Ultrasonic pulse speed and quality of concrete. Source: BS EM 1254-4/04.

Ultrasonic pulse speed (m/s)	Concrete quality
Greater than 4,500 m/s	Great
Between 4,500 and 3,500 m/s	Good
Between 3,500 and 3,000 m/s	Doubtful
Between 3,000 and 2,000 m/s	Bad
Less than 2,000 m/s	Too bad

The dynamic modulus of elasticity can be obtained through Eq. (1) [13].

$$V = \sqrt{\frac{E(1-\mu)}{\rho(1+\mu)(1-2\mu)}} \quad (1)$$

Where:

E = dynamic modulus of elasticity

μ = dynamic Poisson's ratio

p = especific mass

The corrosion potential measurement method measures the negative charge caused by the movement of electrons released by the ferrous ions that move through the electrolyte formed in the concrete, thus providing information about the corrosion status of the reinforcement [14]. "It is a technique widely used for measurements in the laboratory and in the field, due to its practicality and because it requires simple apparatus for its realization, in addition to being a non-destructive technique" [15].

The ASTM-C 876/91 [16] standard establishes the following parameters for the possibility of corrosion in concrete reinforcement based on the corrosion potential measured with copper/copper sulphate semicell, shown in Table 3.

The experimental program was planned to obtain measurements of the corrosion potentials in the prismatic specimens of polymeric mortar for repairs and concrete (as a reference base, and subjected to weekly measurements of the evolution of potential corrosion, after drying cycles (5 days in the autoclave) and wetting (2 days) in a 3.5% NaCl solution.

The concrete was chosen with 24 MPa (trace weight 1: 2: 3 a/c = 0.6 and 344 kg/m^3) because it was the characteristic compressive strength most used for current structures for 30 years, therefore, in buildings that present problems with the corrosion of the armature today.

Table 3 Potential x Probability of corrosion. Source: ASTM - C 876/91.

Corrosion potentials with Cu/SO_4Cu semicell	Corrosion probability
Ecorr < -200 mV	Less than 5%
-200 mV < Ecorr< -350 mV	About 50%
Ecorr > -350	More than 95%

3.1 Characterization of the Materials Used in the Research

Initially tests were carried out to characterize the properties of the materials used in the specimens, according to the norms of the Brazilian Association of Technical Standards-ABNT.

Portland cement CP II F 32 compound with addition of limestone filler between 6% and 10%. Blaine greater than 2,600 cm^2/g, compressive strength > 32 MPa at 28 days [17].

The aggregates for concrete, sand and gravel meet NBR 7211/05 [18].

Industrialized polymeric mortar, cemented with acrylic adhesive agent, one-component thixotropic indicated for being used in structural repairs [19].

Anti-corrosion primer, industrialized based on zinc for metals, composed of synthetic resin and zinc chromate. VOC (volatile organic compounds): 436.32 g/l, used to protect the reinforcement in structural repairs [20].

Anionic corrosion inhibitor primer indicated to protect the reinforcement concrete reinforcement: bicomponent composed of cement modified with acrylic and nitrite-based corrosion inhibitors, free of solvents that acts by inhibiting the anode reaction [21]. AC 60 steel the wires (CA60) are manufactured from wire rod (hot rolled product) with subsequent cold deformation process such as wire drawing or cold rolling. It is a low carbon steel that has a microstructure composed of perlite and ferrite hardened by the cold deformation process [22].

3.2 Characterization of Concrete and Polymeric Mortar

The concrete and polymeric mortar were submitted to immersion absorption tests [23], capillarity absorption [24] chloride diffusion [25] mechanical tests such as compressive strength. The results are shown in Table 4.

Table 5 Characteristics of concrete and polimeric mortar.

Essays/Material	Concrete 1:2:3	Polymeric Mortar
Capillary water absorption (g/cm^2). S = 19.64	0.47	0.26
Water absorption by immersion. 72 hours. Ref (%)	7.96	6.68
Voids index. 72 hours. Ref. (%)	20.8	6.28
Specific mass of the dry sample. 72 hours. Ref (%)	2.16	2.53
Specific mass of the saturated sample. 72 hs. Ref (%)	2.34	2.69

3.3 Accelerated Chloride Induction Corrosion Testing

To meet the research objective, prismatic specimens were molded with 24 MPa concrete and industrialized polymeric mortar for structural repairs, both containing steel bars under three different conditions: without protection, with protection given by zinc-based paints and with protection based on nitrites (Fig. 1).

The steel bars were cleaned with a 1: 1 hydrochloric acid solution with 3.5% hexamethylanetetramine [26]. Then, all the bars were weighed on an electronic scale. One third of the bars were painted with a zinc-based product and another third was painted with a nitrite-based product at a length of 5 cm to be inserted into the concrete or polymeric mortar, leaving 4 cm unpainted to make the connection to the terminal of the measuring device.

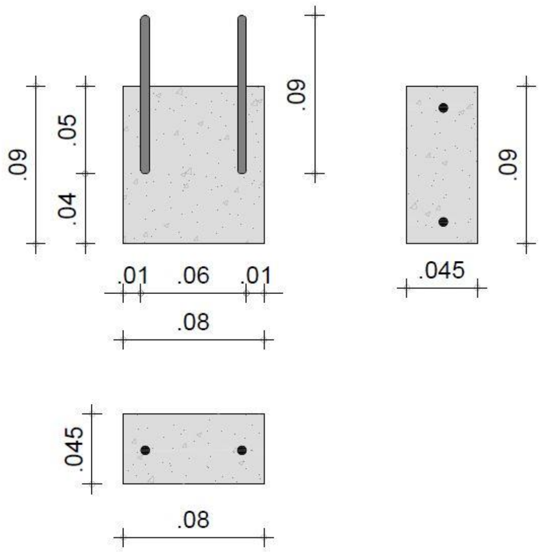

Fig. 1 Sketches of the prismatic specimen.

After molding, wet curing of the specimens was done for five days and 16 days of air curing, the specimens were painted on the base, on the top and on the larger sides, leaving the smaller sides (45×80 mm) unprotected for attack. by the 3.5% NaCL solution. The cycle started on the 24th day of molding, placing them for five days in the oven at 50°C and measuring the corrosion potential. Then, they were placed in a tray containing the solution up to half the height of the steel bars for two days and the corrosion potentials were measured again. This procedure was repeated twelve (12) times. In this way, the corrosion of the reinforcement is induced by the action of chlorides in an accelerated way as verified by several researchers [27-30].

4. Results

The data and results obtained from the tests are presented to characterize the properties of concrete and polymeric mortar.

4.1 Results of Tests for Characterization of Materials

The resistivity of concrete (Fck = 24 Mpa, cement consumption = 344 kg/m^3) was 38.4 kΩ.cm and of polymeric mortar 20.1 kΩ.cm, measured in accordance with the Brazilian standard [31] in age of 61 days, obtained through a device that operates by the principle of the Werner device with the parameters of Table 1 demonstrates that the risk of corrosion in both was moderate. With the ultrasound test [32], the values of the elasticity modules [33] and classification of the quality of the materials were obtained, which are recorded in Table 5.

4.2 Corrosion Potentials

Having established the characteristics of the materials used, it was possible to evaluate the efficiency of corrosion inhibiting coatings and reinforcement coatings when subjected to chloride attack. The chosen method is indicated for offering results with good precision in short periods. Thus, after twelve cycles, data were obtained regarding the evolution of corrosion potentials in the specimens (alkaline concrete and polymeric mortar with unprotected steel bars (SP), with nitrite-based paint (Ni) and base-based paint zinc (Zn), see Figs. 2-4.

Using the spreadsheet tools, the trend line of corrosion potentials is determined for each type of protection for concrete specimens and irons with nitrite and zinc protection. This procedure was repeated in the others. In this way, the deadlines (in days) were determined for the trend line of each protection system to reach — 350 mV (Table 6).

Table 6 Material characteristics.

Material	pulse time	Vp	Vs	BS EM	E	Relation
	μs	m/s	m/s	1254-4/4	GPa	Water/X
Concrete 1:2:3	47.40	4225.00	2191.00	Good	27.28	0.60
Polymeric mortar	51.00	3927.00	2518.00	Good	36.92	0.15

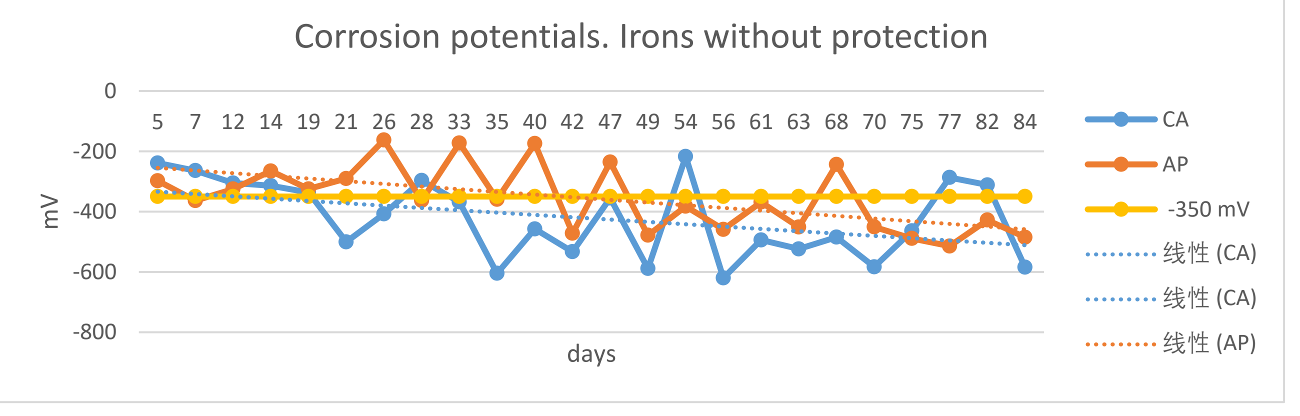

Fig. 2 Corrosion potentials. Irons without protection.

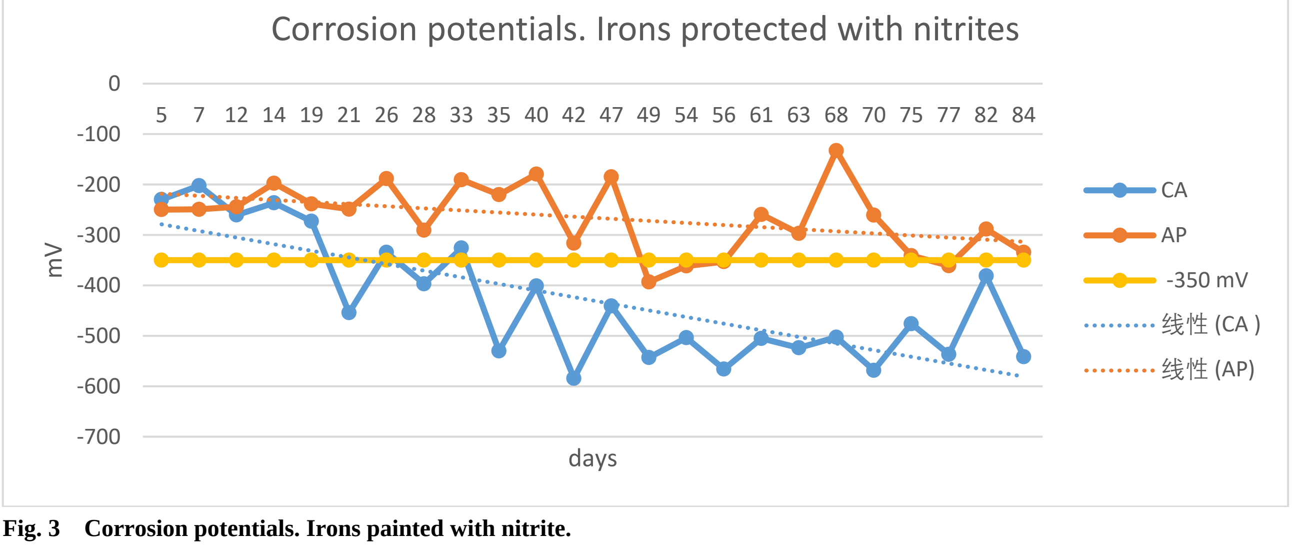

Fig. 3 Corrosion potentials. Irons painted with nitrite.

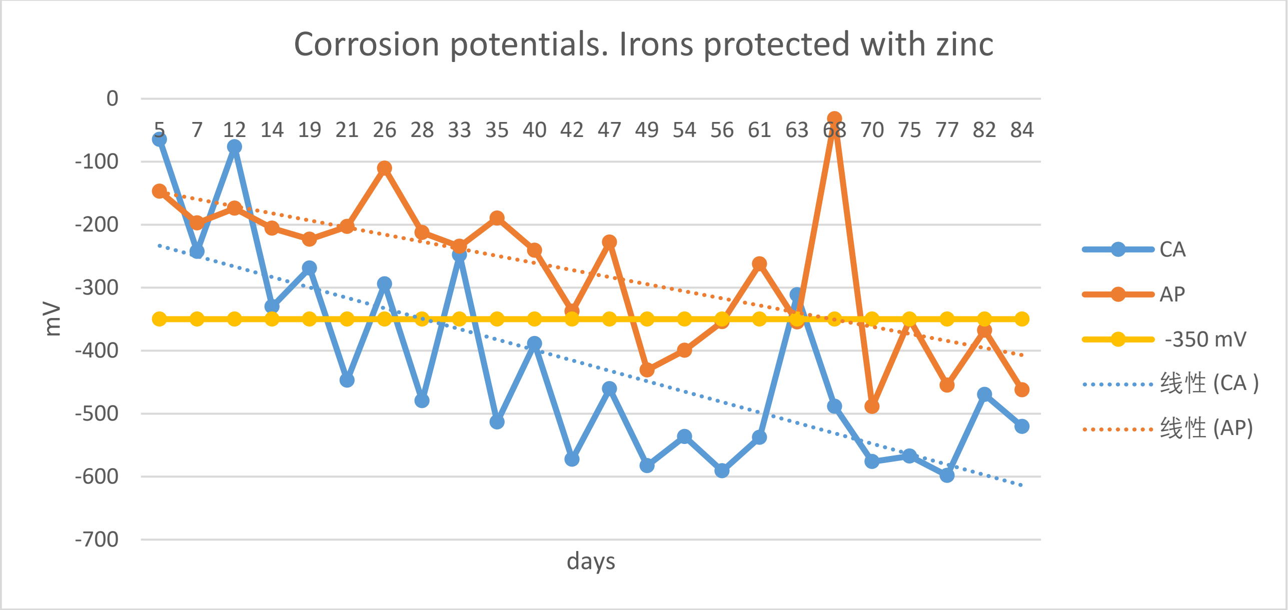

Fig. 4 Corrosion potentials. Irons painted with zinc.

Table 6 Deadlines for the corrosion potential to reach the value of - 350 mV.

Specimen material	Protection of steel bars		
	No protection	With Nitrite	With Zinc
Concrete Fck 24 MPa	12	21	28
Polymeric mortar (AP)	42	Did not reach	68

5. Conclusions

Reinforced concrete structures over time can undergo modifications such as concrete carbonation or interactions with aggressive ions and, therefore, require recoveries that can have high costs and risks. For this reason it is important to research the efficiency and durability of repair materials such as polymeric mortar for concrete and corrosion inhibitors for nitrite-based and zinc-based steel.

In this research, with materials used in structural repair services such as polymeric mortar in the coating and anti-corrosion primers based on nitrites and zinc, it was found that, when subjected to the accelerated chloride corrosion induction test, the polymeric mortar (denser, less voids and water absorption) provides greater protection for steel than 24 MPa concrete (344 kg/m^3 consumption).

However, with protection based on zinc or nitrite, the results are better because the corrosive process in steel is postponed, thus justifying the use of these corrosion inhibitors.

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