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Efficiency of coatings applied on rebars in concrete

W. MORRIS, M. VÁZQUEZ, S. R. DE SÁNCHEZ
División Corrosión, INTEMA, Facultad de Ingeniería, Universidad Nacional de Mar del Plata, J.B. Justo 4302, 7600 Mar del Plata, Argentina
E-mail: surosso@fi.mdp.edu.ar

The performance of three reinforcing steel bars (rebars) coatings is analyzed by means of electrochemical methods. The coatings are representative of those commonly used during the repair of concrete structures affected by corrosion in the coastal regions of Argentina: an epoxy rust conversion coating, a zinc-rich epoxy, and a sprayed zinc coating. Two exposure conditions were investigated: immersed in a saline solution (wet) and exposed to an indoors atmosphere (dry). The rebar corrosion potential (E_{corr}), the corrosion rate (CR) and the electrical resistance (R) between bars were measured during approximately 800 days. In the dry condition the three coatings presented a satisfactory performance characterized by passive E_{corr} values and CR values lower than 1 μm/year. On the other hand, the performance of the coatings in the wet condition depended on their formulations. The rust conversion coating showed active E_{corr} values and CR values higher than those measured on the uncoated bars. The zinc-rich epoxy and the sprayed zinc coatings presented E_{corr} values typical of active zinc. This indicates a certain degree of cathodic protection provided to the reinforcing steel. Besides, R values showed that in this condition, coatings do not provide a barrier type of protection.

1. Introduction

Reinforced concrete is one of the most important structural materials used in the construction industry worldwide. This is primarily due to its low cost, availability, formability, and its excellent structural and durability properties. Nevertheless, certain physical and chemical factors in the service environment can contribute to its deterioration and failure. One of the most significant factors is the reinforcing steel bar (rebar) corrosion.

The high alkalinity of the concrete pore solution that surrounds the steel reinforcement develops a protective layer that protects the rebar from active corrosion. This state is known as passivity and is characterized by a very low corrosion rate. Unfortunately, under certain conditions, the passive state of steel may be lost and the rebar corrosion rate can become significant. Rebar corrosion may occur as a result of concrete alkalinity loss, attack on the steel by aggressive ions, or a combination of both of these factors [1, 2].

Some of the most important variables that influence the rebar corrosion rate are: the structure exposure conditions, the moisture content of concrete, the chemical composition of the pore solution, the concrete porosity and the concrete cover thickness, among others [3–5].

In an attempt to minimize the effect of rebar corrosion, various techniques are frequently employed, such as cathodic protection, inhibitors, and the application of coatings to the external concrete surface or to the reinforcing steel bars. This last option is commonly chosen when repairing reinforced concrete buildings exposed to marine environment, that are affected by rebar corrosion [6, 7]. However, the efficiency of many of these coatings applied to reinforcing steel bars undergoing corrosion is still not well known. A recent investigation presenting short term results of the performance of several concrete and rebar coatings show that under certain exposure conditions the application of some of these products did not affect at all, or even worse, increased the corrosion rate of rebars in concrete [8]. Extensive research performed by Sagüés and coworkers [9] has shown that epoxy coated rebar used in reinforced concrete structures exposed to marine environment may exhibit severe localized corrosion problems on the coatings defects. Thus, we present below a comparative study on the performance of three different coatings: an epoxy rust conversion, a zinc-rich epoxy and a sprayed zinc coating, related to bare, uncoated rebars.

2. Experimental

2.1. Concrete specimen preparation

The samples used in this study consisted of cylindrical concrete specimens containing 8 rebar segments (4 duplicated conditions, see Fig. 1). The rebars have a diameter of 1 cm and present an exposed area of 40 cm^2. Each specimen contains an internal reference electrode (IRE) used to perform the electrochemical experiments.

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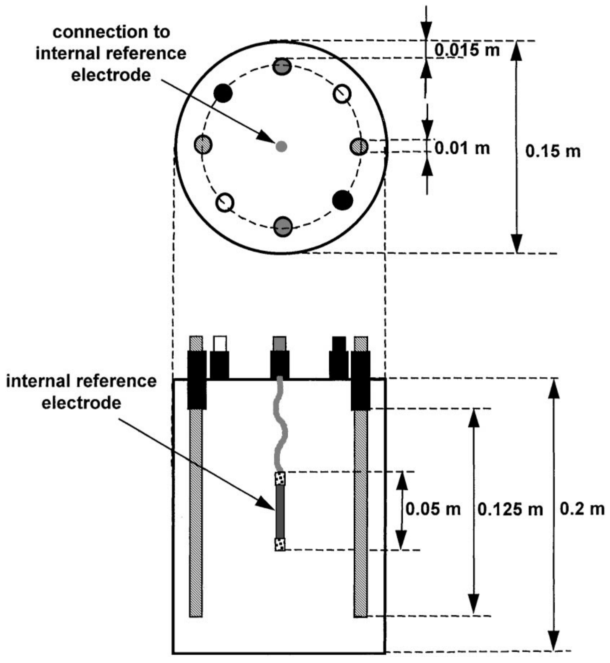

Figure 1 Schematic representation (top view and side view) of the concrete specimen containing the reinforcing bars.

The electrode consisted of an activated titanium rod (0.38 cm of diameter and 5 cm of length) which had its ends isolated with an epoxy resin. This type of reference electrode shows excellent short-term and reasonably good long-term stability in concrete exposed to wet and dry conditions [10].

After curing, the samples were exposed to two different conditions: an indoors atmosphere (approx. 20°C and 60% RH), and partially immersed in aerated 3.5% sodium chloride solution. These two conditions will be referred below as the dry and wet conditions respectively. Duplicate specimens were prepared for each condition. Those labeled 1 and 2 were kept in the dry condition, while those labeled 3 and 4 were immersed in the saline solution 25 days after demolding.

The concrete mix was prepared using a water to cement ratio (w/c) of 0.60 and a cement content of 300 kg/m^3. Crushed stone with a maximum aggregate size (MAS) of 1.27 cm ($^1/_2$ inch), and river sand were used as coarse and fine aggregate respectively. The ratio by weight between coarse and fine aggregate was 1.2. The compressive strength after 28 days of curing was 22.5 MPa (ASTM C-617).

2.2. Coating characteristics

Coating characteristics and the corresponding bar labeling are presented in Table I.

TABLE I Specimen and rebar coating identification

Rebar labelling (duplicated in each sample)	Type of coating	Coating thickness/ μm
S	Uncoated steel	—
E	Epoxi zinc-rich	200
C	Rust conversion coating	250
Z	Sprayed zinc	100

Rust conversion coatings are commercially available products, promoted as able to react directly with a rusted surface to form an inert complex than can be top-coated [11]. The rust conversion coating selected for this study is a one-component epoxy paint containing inhibiting additives based on barium metaborate. This type of coating is representative of the ones commonly used in Argentina during repair procedures of buildings affected by corrosion problems. Following the manufacturer specifications, the coating was manually applied using a brush up to a thickness of 250 μm.

Zinc-rich epoxy coatings are extensively used to protect metallic surfaces directly exposed to the atmosphere. The use of this type of coating is becoming quite common during building repair to prevent further rebar corrosion. However, there is no documented information of its long-term behavior in this kind of application. It has been shown that the zinc content in the paint should be above 90% to guarantee appropriated functioning [12]. Surface preparation and product application followed the instructions provided by the manufacturer. Two hands of paint were manually applied by brush, waiting three days between hands, achieving a thickness of approximately 200 μm.

The sprayed zinc coating was applied on the rebar using a thermal spraying equipment. The rebar surface was previously sandblasted. The coating thickness was approximately 100 μm. This technique is being extensively used to provide cathodic protection to reinforced concrete structures exposed to marine environment [13].

2.3. Electrochemical measurements

The corrosion progress was monitored in time following the variations of the main electrochemical parameters: the corrosion potential E_{corr}, the electrical resistance R, and the polarization resistance Rp. This last parameter was used to estimate the rebar corrosion rate CR.

The corrosion potential was measured using a high impedance voltmeter (HP E2378A) connected to the internal reference electrode (IRE). The readings were corrected against a standard Cu/CuSO$_4$ saturated reference electrode (CSE).

The electrical resistance (R) was measured between bars that presented the same type of coating using a Nilsson 400 soil resistivity meter (see Fig. 1). This instrument uses a square wave of 97 Hz, preventing polarization of the electrodes. The electrical resistance was measured to evaluate the degree of barrier protection provided by each coating and to estimate the electrical resistivity of concrete (ρ) [14]. The values of ρ were calculated as: $\rho = k$. R(S), where $k = 7.5$ and 12 cm for the dry and wet condition respectively, and R(S) is the value of the electrical resistance measured on the uncoated bars expressed in Ω.

Polarization resistance (Rp) was evaluated as $\Delta V/\Delta i$, from potential sweeps up to ± 0.01 V from E_{corr} at a scan rate of 10^{-4} V s^{-1}. Experiments were performed using a CMS100 from Gamry Instruments Inc. potentiostat. The results were corrected to compensate the IR drop error. Rp values where used to calculate the rebar corrosion rates in terms of corrosion penetration (μm year^{-1}). Corrosion rate (CR), in terms of corrosion current density, can be evaluated through polarization resistance according to the Stearn-Geary relationship [15] as:

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} = \frac{B}{R_p} \qquad (1)$$

where β_a and β_c are the anodic and cathodic Tafel slopes respectively, which are kinetic parameters characteristic of each metal-solution system. Due to its dependence on the Tafel slopes, B values should take into account whether the metal is in the active or passive state. Based on polarization resistance and gravimetric measurements, Andrade and coworkers [16, 17] reported typical values of B for plain and galvanized steel embedded in mortar. According to them, the value of B for bare steel in the passive state (typically $E_{\text{corr}} > -0.2$ V) is 0.052 V. The same value of B was obtained for galvanized steel in the passive state (typically $E_{\text{corr}} > -0.6$ V). On the other hand, for bare and galvanized steel in the active state (typically $E_{\text{corr}} < -0.3$ V for bare steel and $E_{\text{corr}} < -0.8$ V for galvanized steel), the corresponding values of B are 0.026 and 0.013 V respectively.

Therefore, B values of 0.026 and 0.052 V were considered for coatings C (rust conversion coating) and S (uncoated steel) in the active and passive state respectively. Likewise, B values of 0.013 and 0.052 V were considered for coatings E (zinc-rich epoxy) and Z (sprayed zinc) in the active and passive state respectively.

Assuming uniform corrosion on the entire bar surface, the nominal value of CR in μm years^{-1} can be calculated using Faraday's law as:

$$\text{CR} = \frac{K a_w}{n F \delta} i_{\text{corr}} = \alpha i_{\text{corr}} \qquad (2)$$

where $K = 315360$ is a units conversion factor, F is the Faraday constant ($F = 96485$ C mol^{-1}), n is the number of moles of electrons transferred, a_w is the atomic weight in grams, δ is the density of the metal in g cm^{-3}, and i_{corr} is the current density in μA cm^{-2}. Therefore, the values of the constant α for steel and zinc are approximately $\alpha_{\text{Fe}} = 11.6$ and $\alpha_{\text{Zn}} = 15$ μA^{-1} cm^2 μm years^{-1} in each case. This approach considers that corrosion takes place on the entire surface of both, the uncoated and coated bars. However, this assumption may underestimate the real corrosion rate on coated bars undergoing localized corrosion on coating defects.

3. Results

Figs 2 and 3 present the evolution of the corrosion potential in time (average of quadruplicate values), for samples exposed to the dry and wet condition respectively. Values for the wet conditions are reported only after immersion. The three coatings and the uncoated bars present a clear tendency that becomes evident after the first 200 days of exposure.

As could be expected, the uncoated rebars in contact with dry concrete present E_{corr} values typical of steel in the passive state, while when concrete is partially immersed in the saline solution, E_{corr} values are characteristic of steel in the active state. As observed in the figures, the bars labeled as C (rust conversion coatings) present a similar behavior than that observed in the uncoated bars (S) for both, the dry and the wet condition. After approximately 600 days of exposure, coatings E and Z achieved average values of E_{corr} of -0.2 ± 0.02 V and -0.36 ± 0.02 V vs. CSE in the dry condition. In the wet condition both coatings present similar trends, achieving E_{corr} values of approximately -0.9 ± 0.04 V. Comparable results have been previously reported for passive and active bare steel and for galvanized steel in contact with dry and wet concrete respectively [16, 18].

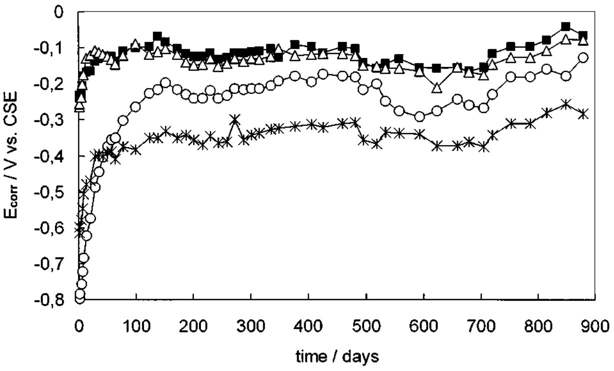

Figure 2 Evolution of the corrosion potential (E_{corr}) in time for specimens exposed to the dry condition (indoors approx. 20°C and 60% RH environment). (■) uncoated rebars, (✳) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

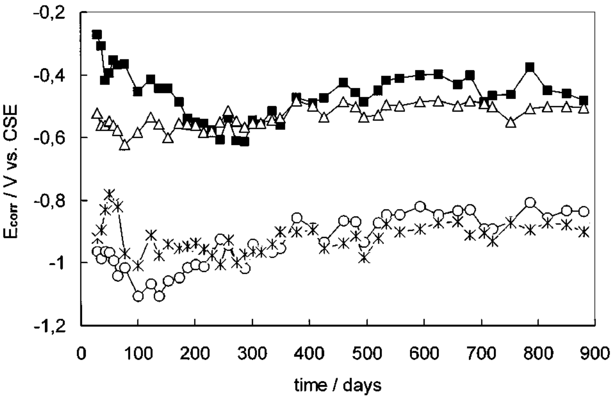

Figure 3 Evolution of the corrosion potential (E_{corr}) in time for specimens exposed to the wet condition (partially immersed in aerated 3.5% chloride solution). (■) uncoated rebars, (✳) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

Figs 4 and 5 show the evolution in time of the electrical resistance (R) for specimens exposed to the dry and wet condition respectively. In the dry condition (Fig. 4) two distinctive tendencies are evident. Coatings C (rust conversion) and E (zinc-rich epoxy) show R values one order of magnitude higher than those measured on uncoated bars and on coating Z (sprayed zinc). Instead, no significant difference is observed between the R values measured on coated and uncoated bars when exposed to the wet condition (Fig. 5). The values of R measured on bars S and Z in the dry condition are approximately one order of magnitude higher than the corresponding values obtained on the wet condition.

At almost 900 days of exposure, the electrical resistivity of concrete achieved values of approximately

100000 Ω·cm and 4200 Ω·cm for the dry and wet condition respectively. These values are consistent with those reported in the literature for similar concrete mixtures exposed to dry and wet environments [18, 19].

Figs 6 and 7 show the evolution of the corrosion current density (i_{corr}) and the corrosion rate (CR) in time calculated as indicated in Equation 2, for specimens exposed to the dry and wet condition respectively. As indicated by Andrade *et al.* [17] and discussed later by Sagües *et al.* [18] the accuracy of the nominal corrosion rate calculations obtained from polarization resistance measurements may range a factor of 2.

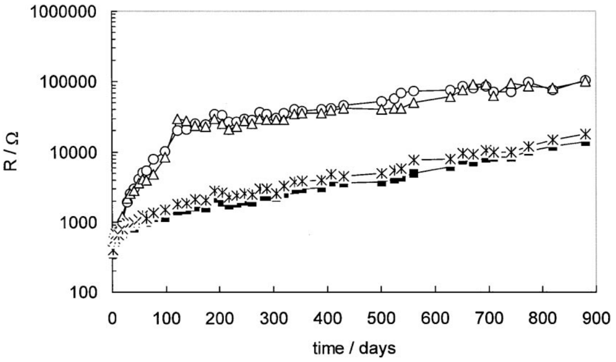

Figure 4 Evolution of the resistance (R) in time for specimens exposed to the dry condition (indoors approx. 20°C and 60% RH environment). Concrete resistivity $\rho = R \times 7.5$ cm. (■) uncoated rebars, (✻) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

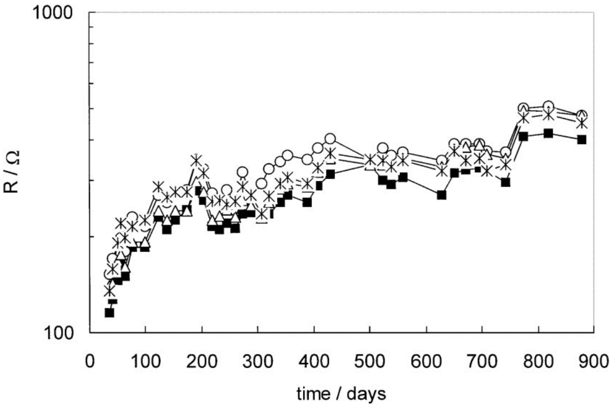

Figure 5 Evolution of the resistance (R) in time for specimens exposed to the wet condition (partially immersed in aerated 3.5% chloride solution). Concrete resistivity $\rho = R \times 12$ cm. (■) uncoated rebars, (✻) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

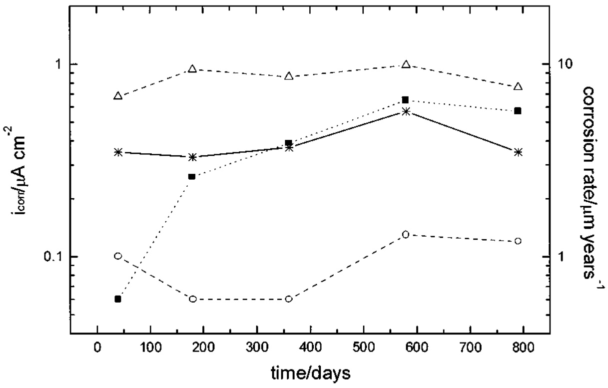

Figure 7 Evolution of the corrosion current density (i_{corr}) and the corrosion rate (CR) in time for specimens exposed to the wet condition (partially immersed in aerated 3.5% chloride solution). (■) uncoated rebars, (✻) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

Taking this fact into account, the values of i_{corr} and CR are represented in a double axis plot even when the conversion factor α_{Zn} used on Equation 5 for bars E and Z (zinc-rich epoxy and sprayed zinc coatings) differs from the value of α_{Fe} used for bars C and S (rust conversion coating and uncoated bars) in a factor of 1.3.

As shown in Fig. 6, the i_{corr} values present a decreasing trend in time for all coated bars in specimens exposed to the dry environment. The uncoated bars presented values of $i_{corr} \sim 0.1$ μA·cm^{-2}, that remained relatively constant in time. This value is consistent with those expected for passive steel in contact with dry concrete [20].

On the other hand, all the specimens immersed in the saline solution, presented an increasing trend in their i_{corr} values, regardless of the type of coating applied on the rebars (see Fig. 7). Furthermore, coating type C (rust conversion) and Z (sprayed zinc) presented higher i_{corr} values than those observed on the uncoated bars.

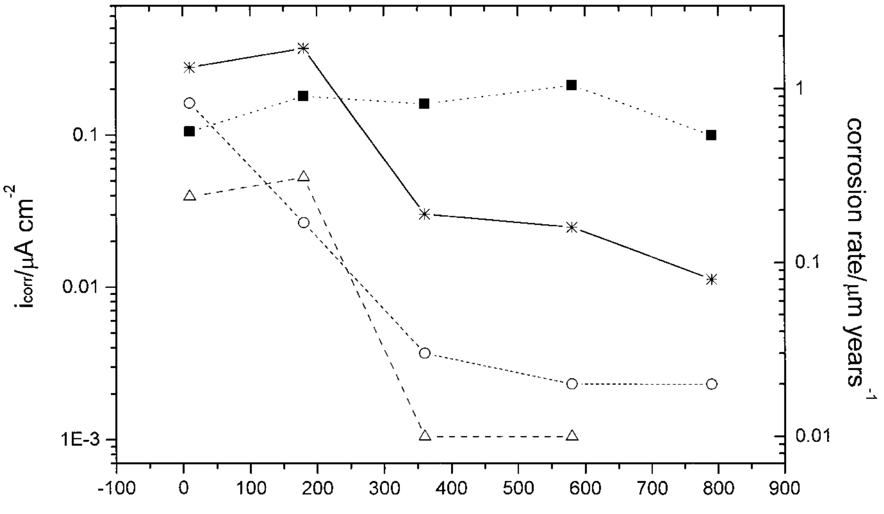

Figure 6 Evolution of the corrosion current density (i_{corr}) and the corrosion rate (CR) in time for specimens exposed to the dry condition (indoors ~20°C and 60% RH environment). (■) uncoated rebars, (✻) sprayed zinc coating, (○) zinc-rich epoxy and (△) rust conversion coating.

As can be seen in these figures, the corrosion rates of both, coated and uncoated bars in contact with wet contaminated concrete is between 1 and 3 orders of magnitude higher than the corresponding values measured on specimens exposed to the dry condition. The most notorious change was observed on bars coated with the rust conversion, that presented a shift of more than 3 orders of magnitude, achieving CR values of approximately $1\ \mu\text{A cm}^{-2}$.

4. Discussion

4.1. General aspects

Coatings may protect reinforcing steel against corrosion by several ways. Most coatings act by providing a barrier that isolates the rebar from the environment. Other coatings contain inhibitor products that modify the environment in contact with the rebar so that steel is passivated or remains in the passive state. A third group of coatings includes those that, in addition to providing a barrier type of protection, also contribute in protecting the rebar by means of a sacrificial type of cathodic protection. The performance and effectiveness of these different types of protection mechanisms can be evaluated in terms of electrochemical parameters.

As described in the previous section, the performance of the different coatings here tested is strongly dependent on the exposure condition of concrete. The difference of almost one order of magnitude between the resistivity values of concrete exposed to the dry and wet condition evidences the increase on the aggressiveness of the concrete when immersed in a saline solution.

4.2. Performance of rebar coatings on dry concrete

On the basis of the results presented above, all coatings showed a satisfactory performance on the concrete specimens exposed to the dry environment. Results of a carbonatation study, performed on concrete specimens prepared with the same mix design than that of this study, show that the carbonatation front reaches the rebar surface after 800 days of exposure. However, the corrosion rates measured on the uncoated bars reveal that rebars continue to show very low CR values, and do not seem to need additional coating protection. Moreover, the high R and low CR values recorded on coatings C and E evidence that these coatings provide an extra barrier type of protection to the already passive steel bars.

As indicated later, bars with coatings E and Z in contact with concrete exposed to the dry condition achieve corrosion potentials values typical of zinc in the passive state. The more positive values of E_{corr} of coating E may be influenced by the continuous dehydration in time of the epoxy matrix that disrupts the contact between the zinc particles. Therefore, the E_{corr} values approach those of bare steel.

4.3. Performance of rebar coatings on wet concrete

When concrete is immersed in a saline solution, uncoated bars achieve active values of E_{corr} and high values of CR. Under these circumstances the performance of the coatings varies considerably depending on the type of protection each one provides.

Bars E and Z (coated with epoxy zinc-rich and spayed zinc) presented a similar behavior in terms of the corrosion potential values. As indicated above, these values are typical of zinc in the active state. Comparing to the E_{corr} values measured on uncoated bars, potential shifts greater than -0.30 V were always measured. This would indicate that coatings E and Z provide a substantial cathodic polarization to protect the steel reinforcement [21].

Conversely to what was observed on coatings C and E in contact with dry concrete, in the wet condition no significant difference in the electrical resistance values is observed between coated and uncoated bars. This behavior clearly shows that under this exposure condition coatings C and E no longer provide a barrier type of protection to the rebar.

As observed in Fig. 7, coating type C (rust conversion) and Z (sprayed zinc) present i_{corr} values that are higher or at least equal than those of the uncoated bars. This behavior would indicate that the corrosion rate of these bars is never lower than the CR values of the uncoated ones. Therefore, a rust conversion coating does not seem appropriated for wet concrete.

5. Conclusions

The performance of rebar coatings used during repair procedures of reinforced concrete structures affected by corrosion is strongly dependent on the aggressiveness of concrete, which can be evaluated in terms of its electrical resistivity.

All coatings showed a satisfactory performance on the concrete specimens exposed to the dry environment. Moreover, the corrosion potentials and the corrosion rates measured on the uncoated bars reveal that rebars remain in the passive state, without needing additional coating protection.

When concrete is immersed in a saline solution the performance of the coatings varies considerably, depending on the type of protection each one provides. Under this exposure condition, no significant barrier type of protection was provided to the rebar by any of the coatings tested.

When concrete is exposed to a wet environment, the rust conversion coating increased the corrosion rate of the reinforcing steel. Therefore, the application of this type of coating cannot be recommended during repair procedures of reinforced concrete structures exposed to wet environment. On the other hand, bars coated with epoxy zinc-rich and spayed zinc presented corrosion potential values typical of zinc in the active state, which gives some indication that coatings E and Z provide a sacrificial type of cathodic protection to the rebar. Further investigations will be necessary to address other aspects such as the protective-ability in the interface coated/uncoated area and the working life of the coatings.

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