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# An evaluation of rust conversion coatings in simulated reinforced concrete pore solutions

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## Keywords

Iron, Alloys, Alkalinity, Corrosion, Chemical properties, Rust

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## Abstract

The performance of reinforcing steel bars (rebars) coated with two different rust conversion coatings was analysed by means of electrochemical methods. Two exposure conditions were investigated, immersion in a pH 14 solution simulating pores in standard concrete, and immersion in a pH 9 solution simulating pore environments in carbonated concrete. The rebar corrosion potential ( $E_{\text{corr}}$ ), the corrosion rate (CR) and the electrochemical impedance ( $Z$ ) were measured over 3 weeks. None of the products investigated helped to improve the resistance of steel against corrosion. Some parameters even indicated a detrimental action, particularly as the alkalinity of the solutions increased. Therefore, the application of this type of coating cannot be recommended during repair procedures of reinforced concrete structures due to the extremely alkaline environment provided by concrete.

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## 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. However, aggressive service environments can contribute to its early deterioration and failure. One of the main factors that influence the performance of reinforced concrete is corrosion of the steel reinforcing bars (rebars).

The high alkalinity of the concrete pore solution that surrounds the rebars determines the passive characteristics of the oxide layer that protects the rebar from active corrosion. Unfortunately, in the presence of aggressive agents, the passive layer on steel may be damaged and rebar corrosion rate can become significant. Rebar corrosion may occur as a result of concrete alkalinity loss, due to CO<sub>2</sub> diffusion, chemical dissolution or weakening by aggressive ions, or a combination of these factors (Schiessl, 1988; Tuuti, 1982).

In an attempt to minimise the effect of rebar corrosion, various techniques can be employed, such as cathodic protection, inhibitors, and the application of coatings to the external concrete surface or to the reinforcing steel bars. Among this last category, rust conversion coatings are commercially available products, promoted as able to react directly with a rusted surface to form an inert complex that then can be over-coated (Deslauriers, 1987). However, the efficiency of many of these coatings when applied to reinforcing steel bars undergoing corrosion has not been extensively researched. A recent investigation presenting short term results of the performance of several concrete and rebar coatings has shown that under certain exposure conditions the application of some of these products did not affect at all or, even worse, could increase the rate of corrosion on rebars in concrete (Morris *et al.*, 2000).

Thus, a comparative study is presented on the performance of two different rust conversion coatings, with and without pigments incorporated to the formulation, applied to bare, uncoated rebars.

## Methodology

### Specimen preparation

The samples used in this study consisted of steel rods of 1 cm diameter cut into 8 cm long segments. The samples were polished with emery paper and then immersed in 3.5 per cent NaCl for 5 h to produce a homogeneously corroded surface, similar to that formed naturally during the storage of steel in marine environments. Some of the samples were then coated, with others remaining uncoated for reference (labelled as G). The rust conversion coating (samples labelled R) was a one-component epoxy paint containing inhibiting additives based on barium metaborate. The other test coating (samples labelled B) was formulated on an alkyd base, and incorporated colour pigments. These types of coatings are representative of the ones commonly used in Argentina when repairing concrete structures affected by corrosion problems. Following the manufacturer specifications, the coatings were manually applied using a brush. The thickness of the coatings was evaluated using a PosiTector6000® meter, giving thickness measurement values of  $40.7 \pm 7$  and  $36.3 \pm 16 \mu\text{m}$ , for coatings B and R, respectively. The measurements were performed at two locations on three different bars. After the coatings dried, both ends of each rebar segment were masked to prevent edge effects, leaving an exposed area of  $15.7 \text{ cm}^2$ .

### Exposure conditions

Two samples of each type (G, B and R) were immersed in solutions simulating the environment found in pores of standard and carbonated concrete. The pH 14.5 solution was prepared with 0.6 M KOH, 0.2 M NaOH and 0.01 M  $\text{Ca}(\text{OH})_2$  (Ramirez *et al.*, 1990) (later referred to as “pH 14 solution”). The pH 9.6 solution consisted of 0.015 M  $\text{NaHCO}_3$  and 0.04 M  $\text{H}_3\text{BO}_3$  (later referred to as “pH 9 solution”). Air was bubbled continuously through the solutions kept at room temperature (approximately  $20^\circ\text{C}$ ). Samples remained immersed in the test solutions for 24 days, this period was chosen to simulate the curing period of freshly-made concrete.

### Electrochemical measurements

The corrosion progress was monitored over time, following the variations of two main electrochemical parameters: the corrosion potential,  $E_{\text{corr}}$  and the polarisation resistance,  $R_p$ . The second parameter was used to estimate the rebar corrosion rate (CR). Polarisation curves were also drawn to evaluate the Tafel slopes, which are kinetic parameters characteristic of each metal-solution system and are needed to calculate the CR. From the curves, the CR was calculated by two other different techniques that are described later. The coatings were also characterised by electrochemical impedance spectroscopy (EIS).

All the electrochemical measurements were carried out using a Solartron Electrochemical Unit 1280 B. A saturated calomel electrode (SCE) was used as the reference electrode and a bronze sheet of large area was used as counter electrode.

The corrosion potential was measured over a 5 min period twice a week.

Polarisation resistance ( $R_p$ ) was evaluated as  $\Delta V/\Delta i$ , from potential sweeps up to  $\pm 0.015 \text{ V}$  and  $E_{\text{corr}}$  at a scan rate of  $10^{-4} \text{ V/s}$ . Polarisation resistance is defined as the slope of the current vs voltage curve in the proximity of the open circuit potential (Jones, 1996). The experimental data could be fitted using a third-order polynomial function (Microcal Origin®, Version 6.0, Microcal Software Inc., 1999).  $R_p$  values were used to obtain estimates of the CRs, in terms of corrosion penetration ( $\mu\text{m}/\text{year}$ ). CR, expressed as corrosion current density, can be calculated from the polarisation resistance according to the Stern-Geary relationship (Stern and Geary, 1957) as:

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

where  $\beta_a$  and  $\beta_c$  are the anodic and cathodic Tafel slopes, respectively.

Assuming uniform corrosion on the entire bar surface, the nominal value of CR in  $\mu\text{m}/\text{years}$  can be calculated using Faraday's law as:

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

where  $K = 315, 360$  is a unit conversion factor,  $F$  the Faraday constant ( $F = 96,485 \text{ C/mol}$ ),

$n$  the number of moles of electrons transferred,  $a_w$  the atomic weight in grams,  $\delta$  the density of the metal in  $\text{g/cm}^3$ , and  $i_{\text{corr}}$  the current density in  $\mu\text{A/cm}^2$ . The value of the constant  $\alpha$  for steel is approximately  $\alpha_{\text{Fe}} = 11.6 \mu\text{A}^{-1} \text{cm}^2 \mu\text{m years}^{-1}$ .

This approach assumes that corrosion takes place on the entire surface of both the uncoated and coated bars. However, this assumption may underestimate the real CR on coated bars undergoing localised corrosion at coating defects.

Anodic and cathodic polarisation curves were recorded, applying potential sweeps up to  $\pm 0.5 \text{ V}$  from  $E_{\text{corr}}$  at a scan rate of  $10^{-4} \text{ V/s}$ . These are considered as destructive tests and the bars undergoing them were discarded after recording each curve. From the  $\log i$  vs  $E$  representation of these curves, the Tafel slopes can be obtained and then the parameter  $B$  (equation (1)) can be calculated. Also, the corrosion current density can be calculated either by extrapolating and intersecting the anodic and cathodic curves or from the extrapolation of any of them to the corrosion potential.

EIS tests were performed on the coated specimens after 24 h and 24 days of immersion in each solution. The amplitude of the signal was  $\pm 0.005 V_{\text{rms}}$  and the frequency varied between 20 kHz and 10 mHz. The results were modelled using an equivalent circuit typical for coated surfaces (Figure 1), where  $C_{\text{dl}}$  represents

the capacity of the double layer,  $R_t$  the charge transfer resistance of the reactions taking place at the metal/solution interface,  $C_c$  the capacity of a perfect film simulated as a non-ideal capacitor (or constant phase element), and  $R'$  the resistance of the defects in the coatings.

This model is based on the assumption that the polymeric coating deviates from the dielectric behaviour because of the ionic conductivity paths generated by the defects.

### Adhesion tests

The tests were carried out following the recommendations in standard ASTM D 3359-93. Two cross-cuts of 1 cm long were made on duplicated specimens. Both coatings could be qualified as 4A. Coating type B, however, was observed to detach easier than coating R while being cut.

## Results

### Corrosion potential

The corrosion potential exhibited stable values after the first 5 min of evaluation. Figures 2 and 3 show the evolution of the corrosion potential over time (averaged quadruplicate values), for samples exposed to pH 9 and 14 solutions, respectively. The steel covered with both coatings exhibited corrosion potential values in the passive range, from the thermodynamic standpoint, and according to Pourbaix Diagrams (Pourbaix, 1965).

Figure 1 Typical equivalent circuit used for modelling the electrochemical impedance spectra of coated surfaces

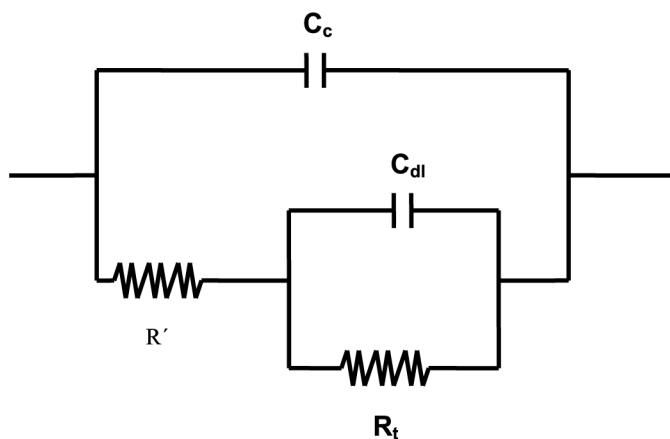
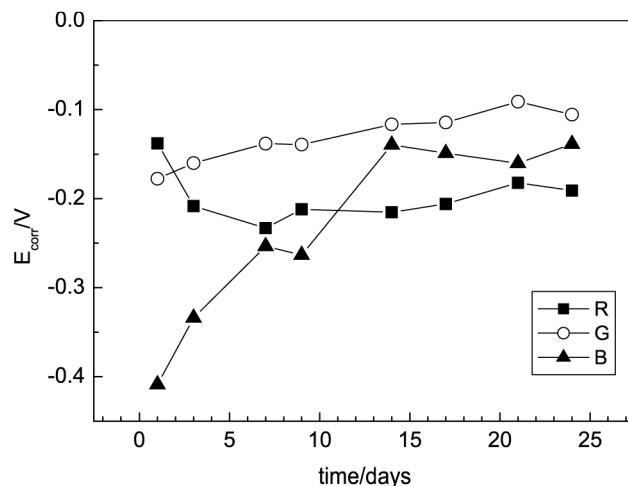
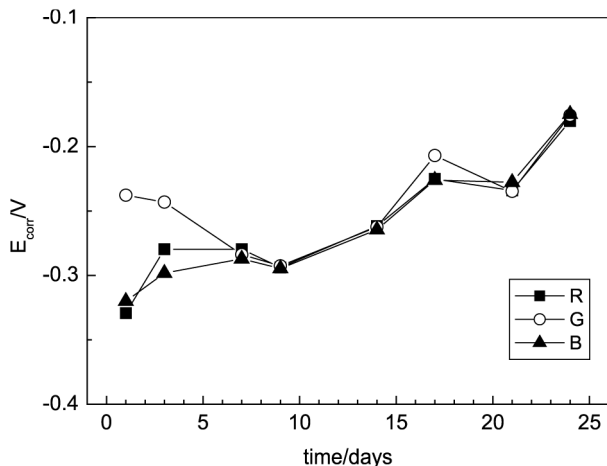


Figure 2 Evolution of the corrosion potential in time for bare and coated samples exposed to pH 9 solution



**Figure 3** Evolution of the corrosion potential in time for bare and coated samples exposed to pH 14 solution



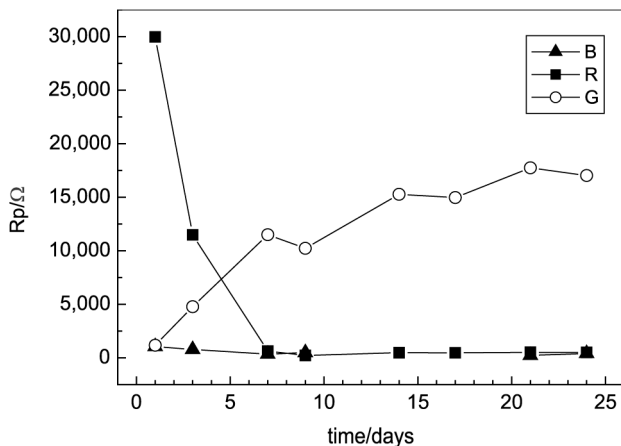
**Polarisation resistance**

Figures 4 and 5 show the evolution of the polarisation resistance over time for the bare and coated bars, immersed in solutions of pH 9 and 14, respectively. As can be seen in equation (1), the  $R_p$  value is inversely proportional to the corrosion current density.

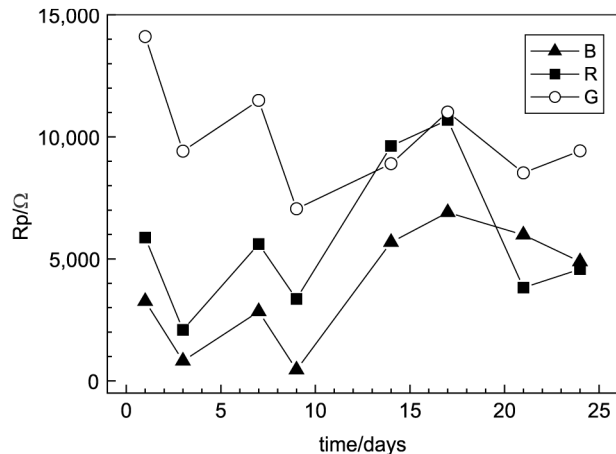
**Polarisation curves**

Anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) were calculated from the semi logarithmic representation of the polarisation curves registered in each experimental condition after the 24 days period of immersion.  $B$  values (equation (1)) were then calculated as shown in Table I.

**Figure 4** Evolution of the polarisation resistance in time for bare and coated samples exposed to pH 9 solution



**Figure 5** Evolution of the polarisation resistance in time for bare and coated samples exposed to pH 14 solution



**Table I**  $B$  values calculated from Tafel slopes of the anodic and cathodic polarisation curves ( $\beta_a$  and  $\beta_c$ ).  
 $B = |\beta_a\beta_c|/2.3(|\beta_a| + |\beta_c|)$

Samples	$B/V$	
	pH 14	pH 9
B	0.021	0.017
R	0.023	0.032
G	0.019	0.046

After the 24-day immersion period, the corrosion current density was calculated in three different ways:

- (1) by intersection of the linear approximation of the anodic and cathodic polarisation curves;
- (2) by reading the current extrapolated from the linear approximation of the cathodic polarisation curve at the corrosion potential; and
- (3) using  $B$  values (Table I) and equation (1).

The percentage of exposed area in the coated specimens was calculated by taking digital images of each bar and analysing them with Scion Image (Image processing freeware, <http://www.scioncorp.com/>). The results are presented in Table II, where the geometrical area ( $15.7 \text{ cm}^2$ ) was taken as 100 per cent. From these values, the corrosion current density was calculated as explained earlier, and the corresponding results are shown in Table III.

**EIS**

Typical impedance spectra (Nyquist format) for coating B are shown in Figure 6. The values calculated from the fitting procedure for parameters  $R'$  and  $C_c$  at short and long immersion periods are summarised in Table IV.

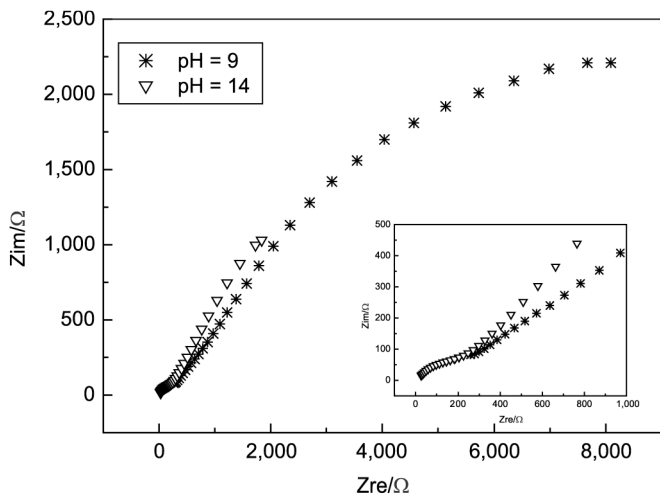
**Table II** Percentage of exposed area in the coated specimens, calculated from the analysis of digital images

Samples	Exposed area (per cent)	
	pH 14	pH 9
B	59	45
R	50	22

**Table III** The corrosion current density calculated by: (a) intersection of the linear approximation of the anodic and cathodic polarisation curves; (b) reading the current extrapolated from the linear approximation of the cathodic polarisation curve at the corrosion potential; and (c) using  $B$  values (Table I) and equation (1)

Samples	Method	$i_{corr} (\mu A/cm^2)$	
		pH 14	pH 9
B	a	0.17	1.56
	b	0.15	2.67
	c	0.45	0.73
R	a	0.41	3.32
	b	0.37	4.85
	c	0.46	0.5
G	a	0.06	0.05
	b	0.07	0.03
	c	0.09	0.52

**Figure 6** Typical electrochemical impedance spectra (Nyquist format) for coating B immersed for 24 days in pH 9 and 14 solutions



Typical impedance spectra (in Bode representation) of bars treated with coating R are shown in Figure 7. Using this form of representation, the polarisation resistance can be calculated by extrapolating the modulus of the total impedance to zero frequency. The results for coatings R and G are summarised in

**Table IV**  $C_c$  (capacity of a perfect film simulated as a non-ideal capacitor) and  $R'$  (resistance of the defects in the coatings) values calculated by fitting the experimental impedance spectra to the equivalent circuit shown in Figure 1. Two immersion times are evaluated for steel samples treated with coating B

	pH 9		pH 14	
	24 h	24 days	24 h	24 days
$R'_E (\Omega)$	93.6	456	277	340
$C_p (\mu F/cm^2)$	0.044	4.630	19.954	38.818

**Figure 7** Typical electrochemical impedance spectra (Bode representation) of steel bars treated with coating R immersed for 24 days in pH 9 and 14 solutions

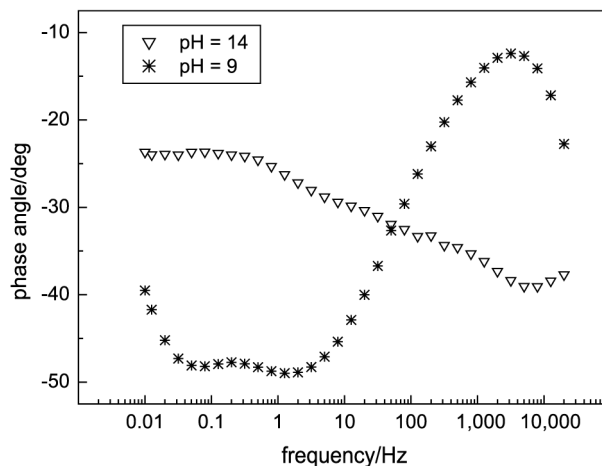
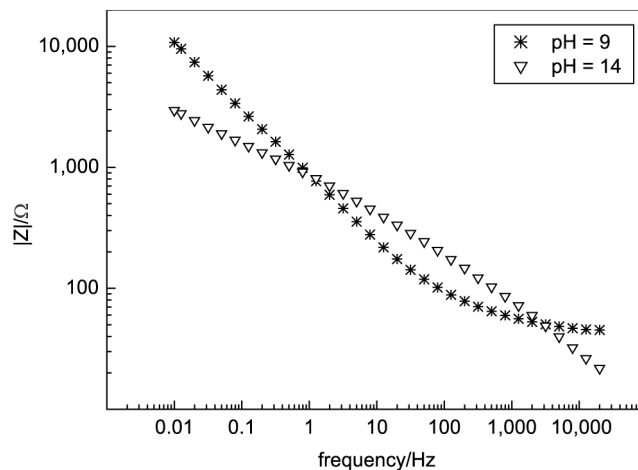


Table V, where they are also compared to the  $R_p$  values calculated from sweeping the potential.

## Discussion

As shown in Figures 2 and 3, the  $E_{\text{corr}}$  values had a tendency to move to more positive values over time. This behaviour can be associated with an increase in the rate of the cathodic half-reaction, due to oxygen diffusion through the coating, or even through blisters and micro cracks. In this last case, the anodic branch rate also may be enhanced and could contribute to the observed shift in  $E_{\text{corr}}$  over time. With regard to corrosion potential values, none of these coatings seemed to provide substantial protection, as compared to the results obtained on uncoated (bare) steel samples. A similar behaviour has been reported earlier for steel embedded in concrete (Morris *et al.*, 2000).

Only during the early stages of the immersion period did the rust conversion coating R show any increase in the polarisation resistance (Figures 4 and 5). However, it has to be considered that there is some scatter in the results from different specimens. As indicated by Gonzalez and Andrade (1982) and discussed later by Sagüés (1996), the accuracy of the nominal CR calculations obtained from polarisation resistance measurements ranges within a factor of  $\pm 2$ .

With regard to the evaluation of the factor  $B$  (equation (1)) that can be used to calculate corrosion currents from polarisation resistance data, it is not surprising that the values presented in Table I differ in a factor of about two from published data, mostly because the latter were recorded in a different environment. Andrade and co-workers (Image processing freeware, <http://www.scioncorp.com/>; Sagüés, 1996) reported typical values of  $B$  for 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, whereas

for steel in the active state (typically  $E_{\text{corr}} < -0.3$  V), the corresponding value of  $B$  is 0.026 V.

The values calculated for the corrosion current density (Table III) were within an acceptable error interval, and those corresponding to uncoated bars agreed well with the values reported in the earlier literature (Morris, *et al.*, 2002). Only the three values shown in the grey cells (Table III) were found to differ in a factor over two, compared to the other values in the same condition.

In the pH 14 solution, the uncoated bars exhibited the lowest corrosion current density values. This clearly shows that the high alkalinity of concrete was sufficiently effective that it could passivate the steel in the time-span covered by these experiments; the presence of a rust conversion coating showed no additional benefit in terms of reducing the overall mass loss. The same analysis is carried out for the solution that simulated rebar conditions in carbonated concrete.

Concerning the impedance results shown in Figure 6, the first semicircle, at high frequencies (see insert in Figure 6), can be attributed to the effect of the coating. In the case of coating B, there was a good correlation between the experimental data points and those fitted using the equivalent circuit presented in Figure 1. On the other hand, the behaviour of the bars treated with coating R could not be modelled by the same equivalent circuit. This coating does not probably provide a barrier type of protection and hence the assumptions of the model fail.

The evolution of  $C_c$  in time (Table IV) provides information on the water uptake, the value being expected to increase in time. The capacitance of the coating increased in both solutions, though the relative increase was lower in the more alkaline solution. This was attributed to the appearance of defects that disrupted the film simultaneously to the hydration process (Table II). This fact would also explain the difference in the values measured for each solution at equal exposure times. In parallel, the increase observed in the values of  $R'$  in time could be ascribed to the fact that the pores in the coating progressively became blocked by the corrosion products, thus increasing the resistance (Peberé *et al.*, 1989).

**Table V** Comparison of polarisation resistance values measured by potentiodynamic polarisation and Bode representation of impedance spectra

		Polarisation resistance ( $\Omega$ )					
R (Bode)		R		G (Bode)		G	
pH 14	pH 9	pH 14	pH 9	pH 14	pH 9	pH 14	pH 9
3,000	$1.0 \times 10^5$	4,400	$1.2 \times 10^5$	3,000	1,800	5,400	3,200

From another viewpoint, the more the decrease in  $R'$  values, the more susceptible to corrosion the interface coating/metal should be.

Additionally, the barrier effect of coating B decreased as the alkalinity of the solution increased.

Finally, the values calculated by extrapolating the impedance results, and directly from the slope of the potentiodynamic curves, compared well and fell within acceptable experimental error (Table V).

## Conclusions

Electrochemical parameters were demonstrated to be appropriate to evaluate the effectiveness of the rust conversion coatings under study in terms of their ability to improve corrosion resistance in solutions of varying alkalinity. The results were in good agreement with visual inspection and exposed area calculations.

Two formulations were selected for this study, and were chosen to represent products that are commonly used when repairing concrete structures with corrosion problems in Argentina. Neither of them improved significantly the behaviour of steel against corrosion, with some of the parameters evaluated even showing an enhancement of the corrosion process, particularly as the pH of the solutions increased. Therefore, the application of this type of coating cannot be recommended when repairing reinforced concrete structures, mainly due to the high alkalinity of concrete.

Under the experimental conditions investigated here, standard rust converters (represented by R), did not even provide a significant barrier type of protection to the steel.

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