

## Electrochemical Realkalisation of Carbonated Concrete: an Alternative Approach to Prevention of Reinforcing Steel Corrosion

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This paper studies electrochemical realkalisation (ER) as a method of preventing steel reinforcement corrosion induced by carbonation. Prismatic specimens of reinforced concrete were made with two types of cement, Portland Compound Cement (CPC) and Portland Pozzolanic Cement (CPP). The specimens were exposed to an atmosphere with 10% CO<sub>2</sub> at 30°C and 65% RH until a partially carbonated concrete was obtained. Then ER was administered for 20 days using 1 A/m<sup>2</sup> of steel and 1M of Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub> solutions as anolytes. During the ER, the pH of the anolyte was measured regularly. In the concrete, besides the application of phenolphthalein, pH was determined at the steel interface and the specimen surface by potentiometric titration in powders. After the treatment, the pH obtained in the specimens made with CPC was higher than that in the CPP, both at the steel interface and at the surface. The type of cement was a variable that affected the pH level reached but the type of anolyte used was not. In the area near the concrete surface, the largest increase in alkalinity was obtained after 5 days of realkalisation, although it should be mentioned that the initial pH considered for a non-carbonated concrete was not reached.

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**Keywords:** Carbonation; Corrosion; Prevention; Realkalisation

### 1. INTRODUCTION

Steel reinforcement corrosion is one of the main causes of maintenance and repairs worldwide [1]. Among the mechanisms of deterioration, corrosion due to carbonation usually occurs in reinforced concrete structures (RC), especially in urban areas, which usually have a high concentration of carbon dioxide emitted into the environment by vehicles or industrial plants. Carbonation (process by which

CO<sub>2</sub> reacts with the alkalis present in the pore solution of the concrete matrix) reduces the alkalinity of the concrete to pH values of 9.0 or less. This process can be accelerated by thin concrete cover, poor compaction, high water/cement or water/cementitious materials ratios, low cement content, and poor curing conditions. When the carbonation reaches the steel reinforcement region, the passivity is broken, thereby initiating generalized steel corrosion. Therefore, the durability of RC structures is subject to considerable changes and reinforcements often start showing signs of decay much earlier than expected for the structure's service life.

Until recently, the most common repair and rehabilitation methods used to increase the service life of RC structures damaged by corrosion induced by carbonation have been the replacement of the element or the removal of contaminated concrete and its subsequent replacement with new alkaline mortar, steel plate bonding, or installation of additional supports [2]. Nevertheless, these procedures have been considered too expensive and technically questionable because of issues related to sustainability and quality of repair. Removal itself can cause problems for both the structure under repair and the structures in the vicinity, e.g. interruption of service, production of dust, or generation of noise. However, it is essential to restore the alkalinity of the pore solution for a carbonated concrete if corrosion is to be prevented.

The electrochemical realkalisation (RE) technique is a non-destructive alternative method based on the application of an electric field to the steel-concrete system. It is considered as a temporary technique because it is applied during a few days to a few weeks. The method basically consists in applying a cathodic current of about 1 A/m<sup>2</sup> to the steel reinforcement by means of a temporary external anode embedded in an alkaline electrolyte. Steel meshes, Titanium-activated meshes, and even mortar paste conductors made with graphite powder, have been used as anodes [3]. The result is the generation of a series of electrochemical, physical, and chemical mechanisms associated with the current flow that can restore alkalinity around the steel bars in the carbonated concrete, thus restoring the passivity of the steel reinforcement [4-6]. OH<sup>-</sup> generation due to electrolysis in the cathodic zone, and electrolyte penetration by absorption and electro-osmosis are the main mechanisms involved.

In this regard, the ER technique has proved it can restore the alkalinity of contaminated carbonated concrete without requiring the removal of the structurally sound concrete [7,8]. However, debate has arisen as to whether the technique is able to achieve repassivation of steel reinforcement that was initially broken by the carbonation of concrete. While pH increase of the concrete may be necessary to achieve the passive state, it is not sufficient to guarantee it. Some studies have used measurements of half-cell potential (HCP) or have made determinations of the corrosion current by potentiostatic or potentiodynamic polarization, or have measured the porosity and electrical resistivity of concrete and the composition of the pore solution without presenting convincing results on the repassivation of steel reinforcement after ER. Laboratory tests conducted to assess the durability of ER have confirmed that, although passive behavior was detected immediately after completion of the treatment, several specimens indicated depassivation after several months of exposure.

Additionally, the effectiveness of the ER technique as a "rehabilitation technique" has been called into question. The term "rehabilitation" should be taken cautiously because as it is known that the structure is not returned to its initial state of health, e.g. the cross section of steel lost by corrosion

is not recovered [9]. For these reasons, this study is based mainly on a strictly preventive application of the ER technique.

ER uses alkaline electrolytes (called anolytes) that are generally beneficial since they facilitate charge transfer and minimize the risk of etching the concrete surface [10]. During ER of carbonated concrete,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  solutions have been frequently used as anolytes and some researchers have used lithium hydroxide [7,11]. Solutions of KOH and NaOH have also been used for realkalisation by means of the absorption-diffusion method [12]. On some rare occasions, tap water has been used [13]. The anolyte solution concentrations usually vary between 0.5 and 1.0 M.

A 1 M sodium carbonate solution has been the preferred anolyte in most of the field and laboratory tests. Some authors claim that, under ambient conditions, it is one of the best electrolytes for ER since it is able to maintain the pH of the anolyte around 10.5 [14,15]. Andrade et al. [6] and Elsener et al. [16] and have shown that the penetration of the  $\text{Na}_2\text{CO}_3$  anolyte from the surface into the concrete pores should prevent pH from decreasing below levels that initiate corrosion. In equilibrium with a constant concentration of  $\text{CO}_2$  in the atmosphere, only small amounts of sodium carbonate will react to form sodium bicarbonate ( $\text{NaHCO}_3$ ), so the additional carbonation leads to only a slight decrease in pH [4,17]. Unfortunately, the introduction of sodium ions may accelerate the alkali-silica reaction (ASR) in the presence of aggregates considered as potentially reactive [17]. Bertolini et al. [18], using  $\text{Na}_2\text{CO}_3$ , reported that the maximum gain of alkalinity was obtained in the vicinity of the steel, affirming that the ER on the external surface of the structure was mainly due to the concrete permeability. Mietz [7] concluded that both diffusion and absorption mechanisms governed the penetration of anolytes through the concrete matrix.

Recently,  $\text{K}_2\text{CO}_3$  has begun to be the more commonly used electrolyte since it provides the concrete with sufficient alkalinity without the risk of developing ASR [17]. Also, it may cause less efflorescence on the treated concrete surface. Hird [19] affirms that the  $\text{K}_2\text{CO}_3$  moves more quickly than sodium, and still conserves its stability at low temperatures.

According to the brief overview above, there is not enough information to understand the role played by electrolytes in the process of realkalisation of partially carbonated concrete structures beyond the fact that they are, by definition, charge transfer facilitators. Issues such as their behavior in the electrical, chemical and physical mechanisms of interaction with different types of cement have not been widely studied. Thus, the objective of this research is to analyze the effect of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  anolyte used in the ER of partially carbonated concrete. The influence of the type of concrete on the ability to recover alkalinity will also be analyzed using two commercial brands of cement commonly used in Mexico. The use of pozzolanic materials, such as fly ash, has become common practice in recent years. This material is a pulverized coal combustion by-product from power plants and is the most extensively used by-product material in the United States [20]. In several Mexican states, some commercial cementitious materials may include two or more pozzolanic additions. Such is the case for Portland compound cement and Portland pozzolanic cement (named CPC and CPP, according to NMX C 414 [21]). The content of pozzolanic materials in the composition of these types of cements is variable and they can replace up to 50% of the ordinary Portland cement (NPC/OPC type I, according to ASTM C 150 [22]).

Thus it has been found that several factors have an impact on the efficiency of ER, some of them attributable to the microstructure of concrete, and others inherent in the technique itself. Generally speaking, the majority of ER-related studies have been conducted in fully carbonated concrete. However, under the assumption that the ER should be applied as a preventive method [9], the approach of this research focuses on concrete presenting partial carbonation, e.g. where the carbonation front (revealed through the phenolphthalein technique) has not reached the steel reinforcement. In this way, we expect to avoid problems associated with uncertainty regarding the repassivation of steel, since concrete located in the region near the steel-concrete interface would be healthy. The study is focused on the analysis of the supplied voltage, pH evolution in both the anolyte and the concrete, the movement of cations, and the potential behavior of steel reinforcement before, during and after the ER application.

## 2. EXPERIMENTAL PROGRAM

### 2.1 Materials

Two commercial grade Portland cements called CPC and CPP (CPC-30R and CPP-30R according to NMX-C-414-ONNCCE, and respectively, CEM II/B and CEM IV according to EN 197-I:2011 [23]) were used in the concrete mixtures. The chemical composition of the cements used in this research program is presented in Table 1. Concrete mixtures were prepared with calcareous aggregates and their compositions corresponded to those of common concrete constructions. The compositions are presented in Table 2. The average 28-day compressive strength of the concrete was 24 MPa for CPC and 26 MPa for CPP.

**Table 1.** Chemical composition of cements used.

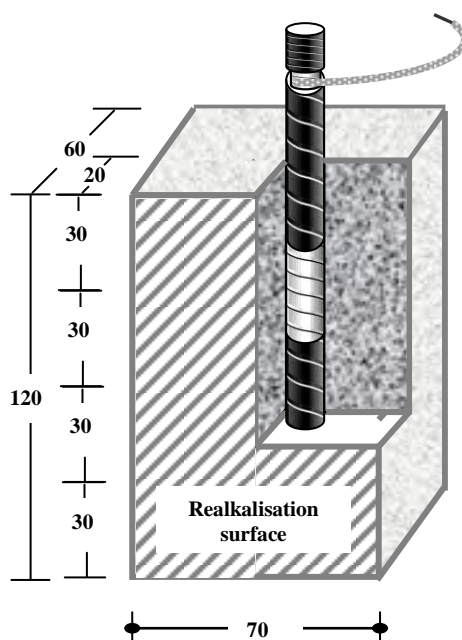
%	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> Oeq	LOI
CPC-30R	59.5	16.9	4.3	1.6	3.39	1.5	0.72	0.41	0.18	0.04	0.88	7.3
CPP-30R	52.1	29.8	6.8	3.0	2.6	1.4	1.26	0.73	0.21	0.11	1.56	2

**Table 2.** Concrete composition for test specimens.

CPC/ CPP	352 kg/m <sup>3</sup>
Calcareous Sand (0/4 R)	665 kg/m <sup>3</sup>
Calcareous Gravel (nominal maximum size =10 mm)	1025 kg/m <sup>3</sup>
Water	229 L/m <sup>3</sup>
W/C	0.65

## 2.2 Preparation of specimens

Prismatic concrete specimens measuring 60 x 70 x 120 mm were cast with an embedded steel rod 10 mm in diameter (see Fig. 1). Industrial grade A60 steel according to ASTM A370 [24], and designated G42 according to NMX-C-407-ONNCCE [25], was used. This steel bar was positioned so as to achieve a critical cover depth of 20 mm from one of the specimen faces (named “realkalisation” surface) and a cover depth of 30 mm with respect to the remaining faces. Before the steel bar was used, its surface was cleaned chemically and a polymer resin was applied to it, leaving a 30 mm length in contact with the concrete.



**Figure 1.** Schematic representation of specimens for ER (all dimensions are in mm).

The specimens were cast and then stored in a curing room at 20°C and 95% RH for 24 h. After this period, the specimens were demolded and cured at 20 ± 1 °C and 100% RH for 28 days.

## 2.3 Exposure conditions

After the curing period, the specimens were placed in an environmental chamber at 40 °C with a relative humidity of 60 ± 5% for 7 days, which ensured the optimum humidity level for the development of carbonation reactions.

After this, the test specimens were placed in an accelerated carbonation chamber at T= 30 ± 2°C, RH= 60-70% and a CO<sub>2</sub> concentration of 10 ± 1%. The exposure time was measured from this point. With regard to time, two specimens were removed from the chamber and the carbonation depth

was measured by spraying phenolphthalein on to a freshly split surface of each of the prismatic specimens.

This procedure continued until a carbonation depth of 14 – 16 mm of concrete was obtained (in this study this is called "partial carbonation" of the concrete). Thus, the preventive effect of ER was analyzed.

#### *2.4 Electrochemical realkalisation treatment*

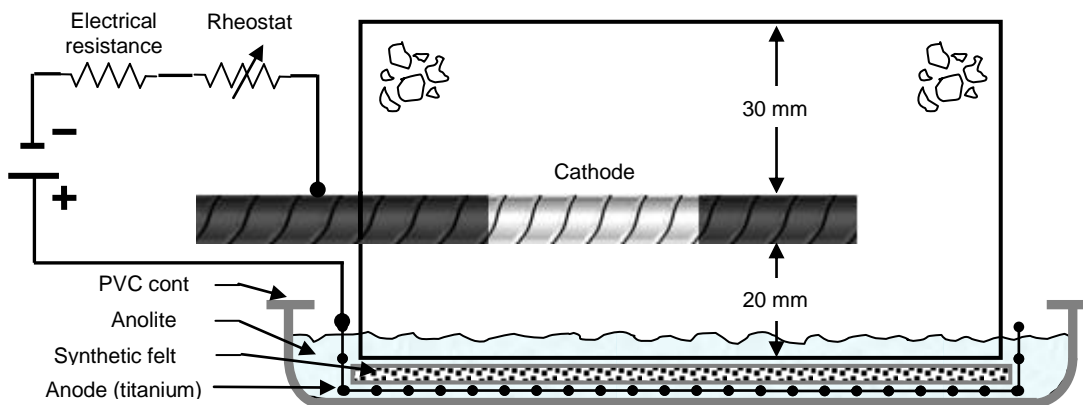
The ER technique was applied as follows. Titanium mesh anodes were fixed on the specimens parallel to the realkalisation surface to provide the electrical contacts (Fig. 2). The specimens were then placed in PVC containers. The partial immersion of the realkalisation surface of the specimens reduced their electrical resistance and, consequently, the problems of current or voltage limitations were overcome.

For each type of cement, two series of specimens were subjected to ER: one series with  $\text{Na}_2\text{CO}_3$  and the other with  $\text{K}_2\text{CO}_3$ , both at concentrations of 1 M. In all cases, the anolyte volume remained constant throughout the ER. A constant current of 1 A/m<sup>2</sup> of steel reinforcement was applied between the two electrodes (rebar and titanium mesh anode) for 20 days. An electrical resistor of 1  $\Omega$  was connected in series with each specimen so that the amount of current applied could be constantly verified (using Ohm's law). It was also necessary to connect a rheostat in series in order to regulate the current selected.

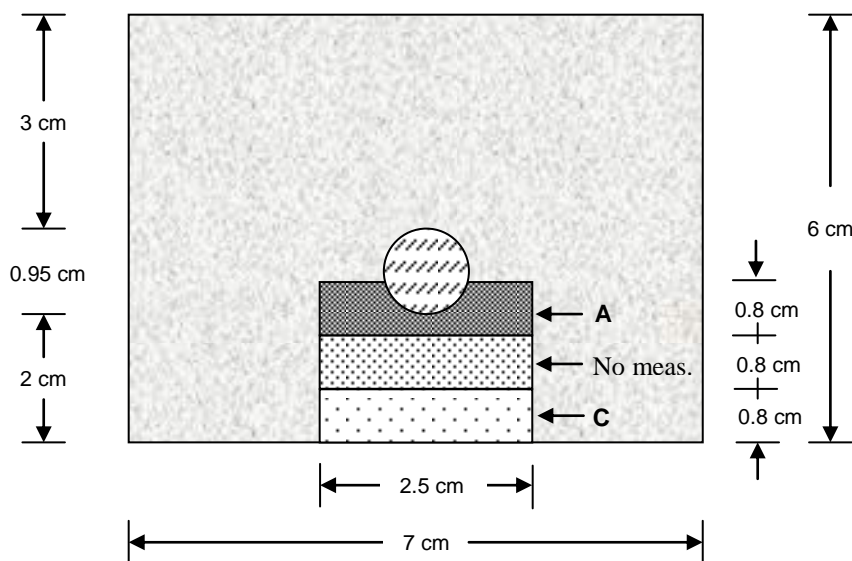
#### *2.5 Measurement methods*

During the ER application, the potential difference between anode and cathode was measured regularly. Also, the pH of the anolyte and of the concrete was measured before and during the ER. For this, some specimens were disconnected regularly and subjected to the tensile splitting test in order to examine the state of corrosion of the rebar and to determine the realkalisation depth by applying phenolphthalein to a freshly split surface.

At the same time, in order to track the pH evolution of the concrete, samples were taken in two different regions of the concrete cover, as shown in Figure 3. The region "A" corresponded to concrete located close to the steel-concrete interface (~ 5 mm) and the region "C" represented the concrete located between the specimen surface and up to 8 mm into the cover depth. The concrete samples were pulverized to <100  $\mu\text{m}$ . Solutions were prepared by dissolving the obtained powder in water at a powder/water ratio of 1/10, according to the procedure described in the literature [26]. The pH was then measured by potentiometric titration. In region A, chemical analysis to determine the sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) ion content was also performed after acid digestion [27]. The dissolved alkalis were quantified by atomic absorption spectrometry. The steel potential was recorded before and after application of ER to determine the time of depolarization of the steel – concrete system and the state of steel reinforcement corrosion.



**Figure 2.** Scheme of the setup of the experiment.



**Figure 3.** Schematic representation showing regions of the taking samples procedure of concrete. Intermediate region between A and C was not measured. All dimensions are in cm

### 3. RESULTS AND DISCUSSION

#### 3.1 Phenolphthalein indicator test

The use of the phenolphthalein indicator was one of the more conventional methods utilized to evaluate the ER effectiveness. Figure 4 shows the result of the application of phenolphthalein to fresh pieces of CPP concrete specimens before and during the ER. A similar pattern was found in the concrete specimens made with CPC.

Time (days)	Electrochemical Realkalisation (ER) with the two analytes	
	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>
Prior to ER		
5		
9		
13		
17		
20		

**Figure 4.** Results of phenolphthalein spraying on fresh fracture of specimens named CPP taken at 0, 5, 9, 13, 17 and 20 days of realkalisation.



In all cases, the realkalisation surface is at the bottom of the images. Prior to the ER, two areas clearly showed the partial carbonation of the cover depth of concrete obtained after induction of carbonation. The average depth of carbonated concrete was 15 mm.

During the time of the ER application, a recovery was observed in the concrete alkalinity, mainly from the contact surface between the anolyte and the specimen. In this case, the application of phenolphthalein showed progression of the realkalised depth. After 13 days of ER application, the initial carbonated region was observed to present a pink hue, demonstrating an increase in the pH of the concrete to above 9.5 in this region. This can be attributed to absorption, diffusion and electroosmotic flow phenomena [7]. In contrast, as can be seen in the different images of Figure 4, the size of the initial non-carbonated area in the vicinity of the steel reinforcement did not appear to undergo any significant changes during the ER.

Despite the evident changes, the conventional method using phenolphthalein could only distinguish whether the pH was higher than 9 or not, but could not differentiate pH values further. Samples of concrete powder were therefore taken and their pH was determined by titration. As will be commented later, a slight increase in the pH value was observed in the area near the steel-concrete interface, due to OH<sup>-</sup> generation.

### 3.2 Driving voltage measurements

The evolution of the potential applied between the steel reinforcement and the titanium mesh for CPP and CPC specimens is presented in Figure 5.

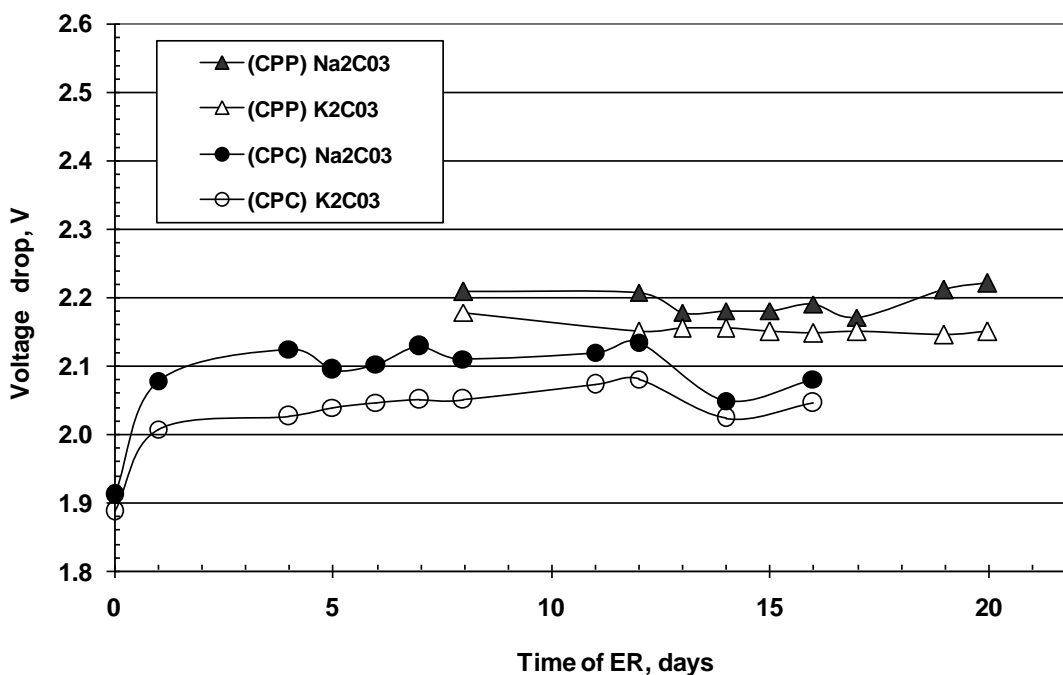


Figure 5. Evolution of voltage drop between anode and cathode

The influence of the type of anolyte used is also shown. It can be observed that, during the ER, the potentials applied between the anode and cathode were slightly higher in the specimens treated with anolyte  $\text{Na}_2\text{CO}_3$ , regardless of the type of cement. This behavior could be attributed to the relatively higher ionic conductivity of  $\text{K}^+$  ( $73.5 \text{ ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ ) relative to  $\text{Na}^+$  ( $50.1 \text{ ohm}^{-1}\text{cm}^2\text{eq}^{-1}$ ). On the other hand, it was found that, in specimens made with CPP, the potential applied between the anode and the cathode was 5.5% higher than that applied to the CPC specimens. An explanation of this behavior could be related to the difference in the resistivity of the specimens (measured prior to ER application by means of the Electrochemical Impedance Spectroscopy technique in accordance with Fajardo et al. [28]). In this regard, it was found that the resistivity was  $22.4 \text{ k}\Omega\cdot\text{cm}$  for CPP and  $7.7 \text{ k}\Omega\cdot\text{cm}$  for CPC.

### 3.3 pH-value of anolyte and concrete bulk

There is limited literature on the pH behavior of the different anolytes used in the application of ER. Some standards and patents [10,15,19] are restricted to controlling pH in the anolyte, particularly when catalyzed titanium anolytes are used. In these cases, it is mentioned that the anolyte should be protected by means of periodic solution additions, in order to prevent the anolyte pH from decreasing to 7. As can be seen in Figure 6, the pH evolution in the anolytes during specimen realkalisation may provide further observations.

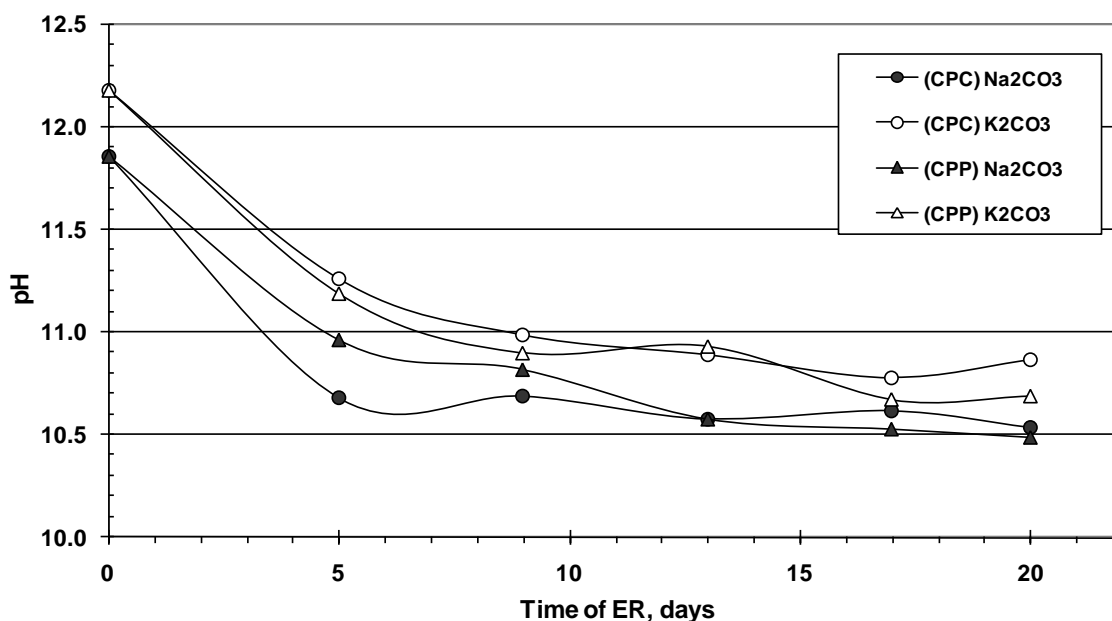


Figure 6. pH-values obtained in the anolytes during ER.

In fact, in Figure 6 it can be seen that the  $\text{K}_2\text{CO}_3$  pH remains above that of the  $\text{Na}_2\text{CO}_3$  anolyte throughout the test period. During the first 5 days of ER, a fast decrease can be observed in pH

regardless of the anolyte used. However, from day 5 until the end of the ER application, a relatively stable pH is shown, reaching values between 10.5 and 10.8 for both anolytes used. In the case of  $\text{Na}_2\text{CO}_3$ , similar pH values have been found in other works [7,29]. The decrease can be attributed to two phenomena. First, theory holds that two substances with different pH, when in contact, tend to reach equilibrium. In this case, when the anolyte is in contact with the concrete pore solution, both solutions tend to the equilibrium mentioned above. Second, water oxidation, a phenomenon evidenced by bubbles observed in the anodic region, occurs as reported by Andrade et al. [6]. In this regard, in a study on entirely carbonated probes and using  $\text{Na}_2\text{CO}_3$ , it was found that the decrease in the anolyte pH was directly related to the current density and the period of application [30]. In this work it was observed that, without refreshing or change of the anolyte during the experiment, and using current densities of  $2 \text{ A/m}^2$  during 20 days of application, the pH of the anolyte decreased to 9.6.

As mentioned above, the purpose of the ER is to restore the pH of the pore solution close to the steel-concrete interface by creating the optimum conditions for rebuilding and maintaining a durable passive layer. The pH-value reached after the ER is taken as one of the two end point criteria in SP0107 [10]. The effectiveness of the ER process is demonstrated indirectly by pH testing using the phenolphthalein method. Regarding the results shown in Figure 4, starting on day 13 of the ER, the concrete of the specimens turned the indicator pink, which should mean realkalisation. Additionally, in order to obtain a quantitative parameter, the pH distribution was determined in two regions situated perpendicularly to the realkalisation surface (A and C in Figure 3) between the two electrodes (see Figures 7 and 8).

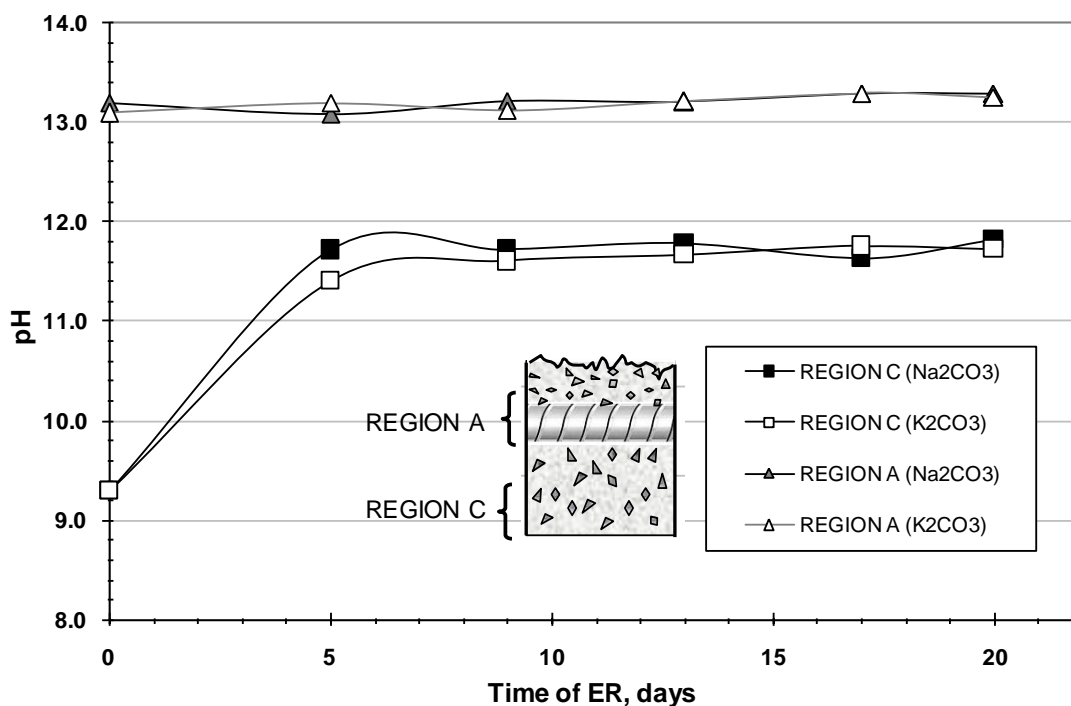
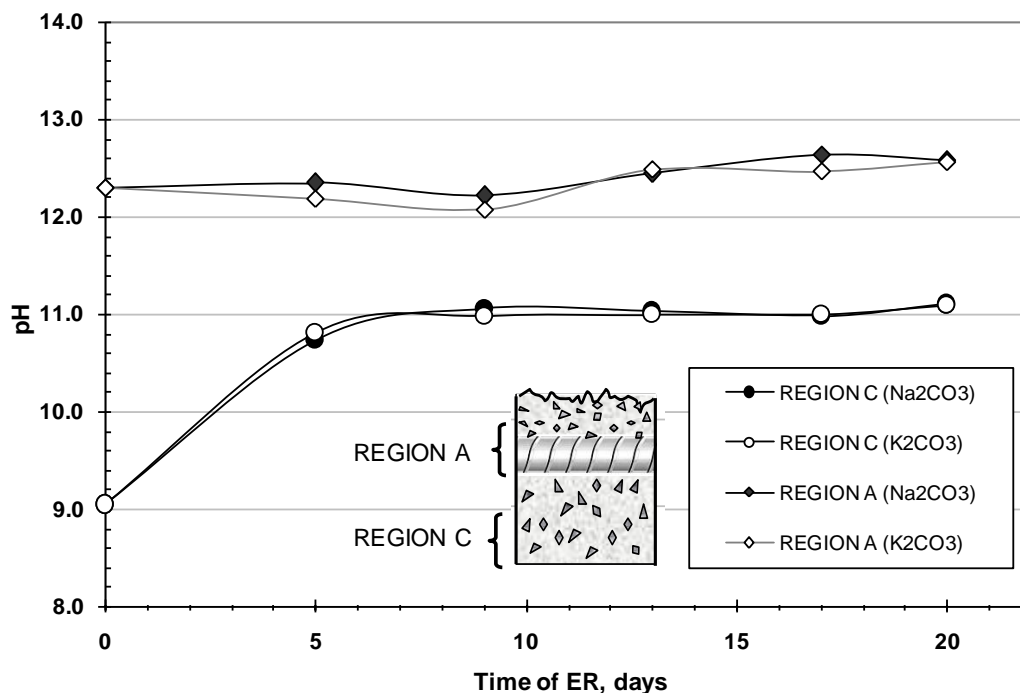


Figure 7. pH-values obtained in the concrete matrix for CPC specimens.



**Figure 8.** pH-values obtained in the concrete matrix for CPP specimens.

In this case, in region C, a considerable increase in the concrete pH was found during the first 5 days of ER. Subsequently, the pH values tended towards an asymptote regardless of the type of concrete used. This behavior is consistent with that recorded in the evolution of the anolyte pH, which presented a constant value after 5 days of ER. However, concrete realkalisation was not reached until day 13 of the application.

Towards the end of the ER, it could be observed that, for CPC, pH was 13.2 and 11.8 in regions A and C respectively (Figure 7) while, for CPP, pH was 12.6 and 11.1 for regions A and C respectively (Figure 8). Results show that, in region C, ER increased the pH value of carbonated concrete to values slightly higher than 11. However, the original value of sound concrete could not be recovered (13.2 and 12.2 for CPC and CPP respectively). From the results obtained, it can be inferred that, in the treated concrete and for the analyzed areas A and C, the evolution of pH is not influenced by the anolyte used.

In regions A and C, it was noted that the pH of the CPP concrete specimens was lower than that of CPC. Pozzolanic concretes have long been considered to be less capable of resisting carbonation than normal Portland cements owing to their lower portlandite content [31]. In pozzolanic concretes, like CPP, the amount of  $\text{Ca}(\text{OH})_2$  is significantly reduced by the lower quantity of clinker and consumption by pozzolanic reaction [32-34] during hardening of the concrete, thus reducing the alkalinity of the pore solution [35]. However, it can be concluded that the application of ER allowed an increase in the alkalinity of concrete near the steel-concrete interface. This is evidenced by the increase of the pH in region A. Regarding this, Hondel et al. [36] applied ER to concrete specimens made with ordinary Portland cement and blast furnace slag, finding that, in order to reach a similar realkalisation

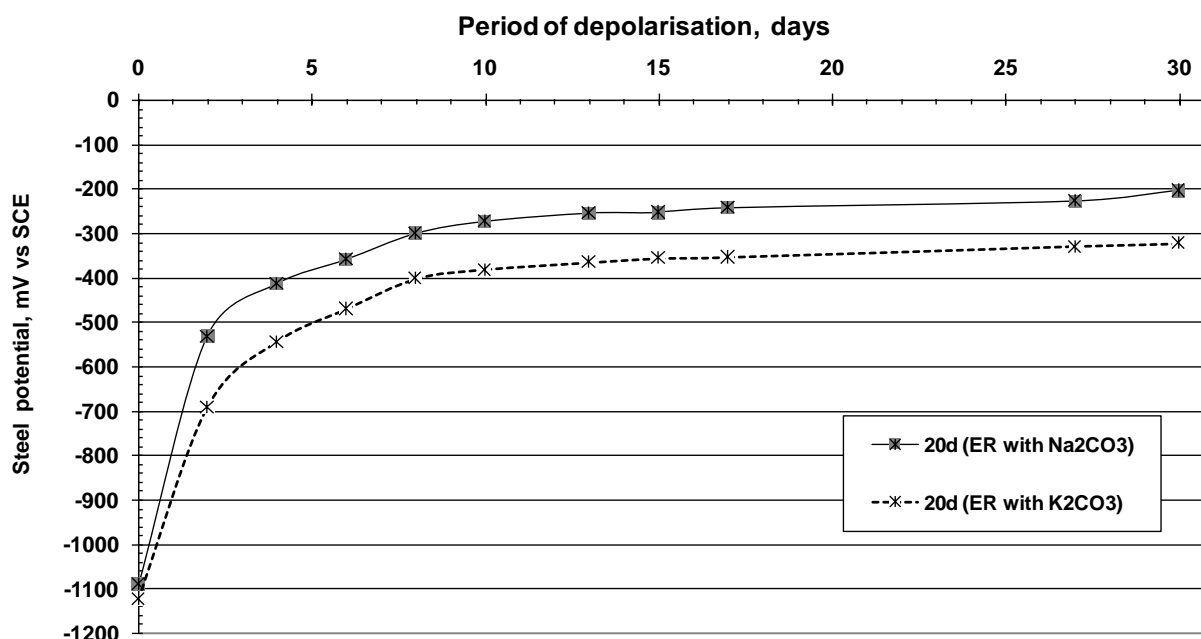
level in both concrete types, it was necessary to increase the total current flow in those made with slag. Nonetheless, in this work, the results obtained in partially carbonated concretes would indicate that, at the steel–concrete interface, the pH value was constant, or could be increased as in the case of specimens made with CPP without elevating the current flow. This could be considered a favorable effect in terms of energy saving and in a small recovery of alkalinity initially lost due to the pozzolanic effect. In some countries, the use of pozzolanic materials in addition to or as substitutions for Portland cement has become common practice. In central and southern areas of Mexico, pozzolanic Portland cement is commercialized and the NMX C414 standard [21] allows substitution of up to 50% of clinker by pozzolanic materials.

Only a few papers in literature report an increase in the pH of concrete to values above 12.5. In our case, we think the alkalinity obtained in the area near the steel reinforcement (region A) would be strengthened given that the concrete is healthy (i.e. without carbonation). Therefore maintained or slightly increased alkalinity would help to reinforce the stability of the passive layer. Likewise, resistance to further carbonation would be significantly raised as the entire alkalinity is also elevated with the increase in alkali content. Table 3 presents the results for the cation content ( $\text{Na}^+$  and  $\text{K}^+$ ) of specimens realkalised with  $\text{K}_2\text{CO}_3$  in which the increase in sodium and potassium ions around the steel-concrete interface is noted.

### 3.4 Corrosion results

During ER treatment, a voltage is applied between the anode and cathode in order to obtain the current that satisfies the previously established criterion ( $1 \text{ A/m}^2$ ). This elevated cathodic current changes the potential of steel reinforcement in concrete to negative values. Figure 9 presents the results measured for the depolarization of specimens made with CPP after the end of the ER (after 20 days of application). In this Figure, time  $t=0$  refers to the beginning of the depolarization or post-treatment period immediately after disconnection of the specimens.

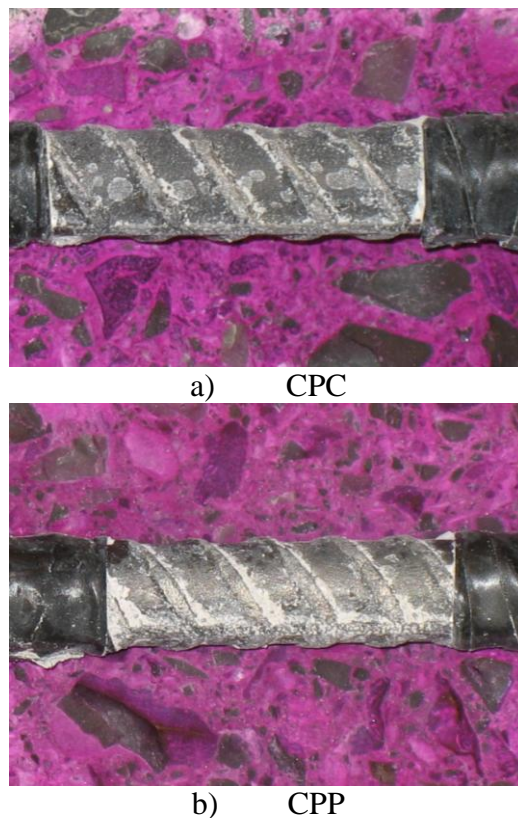
As reported in other works [7], immediately after the specimens were disconnected ( $t=0$ ), values near to  $-1.1 \text{ V}$  (vs SCE) were measured. After one day of depolarization, values remained in the range of  $-650$  to  $-900 \text{ mV}$  (vs. SCE). As can be seen in Figure 9, steel depolarization records show that the values measured on the treated area remained homogeneous from day 9 to day 30, at around  $-200 \text{ mV}$  and  $-340 \text{ mV}$  (vs. SCE) for CPP specimens realkalised with  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  respectively. In our case, the relatively homogeneous potential obtained after the treatment could be considered a strong indication of depolarization of the steel-concrete system. The time required to achieve a homogeneous potential can be at least 7 days and some studies have reported up to 30 days [37]. It was found that the specimens realkalised with  $\text{Na}_2\text{CO}_3$  became depolarized relatively faster. This can be attributed to the difference of the applied potential on the specimens realkalised with this anolyte (see Figure 5). An important feature of this research is the period in which the specimens remained polarized (12 to 15 days in both cases). According to Green et al. [38], the relatively porous matrix of the specimens ( $w/c=0.65$ ) allows oxygen to enter and become available at the steel reinforcement surface, resulting in its rapid depolarization.



**Figure 9.** Steel potential of CPP specimens measured during depolarization period.

This parameter provides an indication of the time when the electrochemical measurements could be considered as reliable, i.e.  $R_p$  measurements,  $E_{corr}$ , EIS.

Despite the relatively fast attainment of electrical equilibrium of the specimens, it appears that the measurements of the steel reinforcement potential may reflect a high probability of corrosion, particularly in the case of specimens realkalised with  $K_2CO_3$  (steel potential  $< -250$  mV vs. SCE). The experimental conditions established here presuppose that the embedded steel reinforcement was protected, as the concrete around it remained free of carbonation at the time of the ER application (as evidenced in Figure 4). In this respect, the values of the steel potential obtained here, even after complete depolarization, cannot be easily interpreted in terms of the thermodynamic stability of the passive layer and the consequent chemical protection conferred by the concrete. This contrasts with the physical state of the steel reinforcement shown in Figures 10a and 10b after the ER application. In those figures, it can be clearly observed that there are no traces of corrosion on the steel surface. Additionally, the pH of concrete near the steel-concrete interface was 12.5 for CPP and 13.2 and for CPC specimens. The uncertainty on the measurements of the steel potential (according to ASTM C 876 criteria) would be related to factors affecting the measurements [39]. In particular, the moisture content and resistivity of concrete are directly affected by the conditions during the measurement. In accordance with the conclusions expressed by Odden [40], it might be thought that a strict interpretation would be difficult without calibrating the specimens: in the case of structure treated with ER since the application of the electric field, the introduction of ions and the measurement conditions change the chemical, electrochemical and dielectric properties of concrete. The results obtained could be considered for a possible study in the future, the objective of which might be the calibration of the corrosion thresholds.



**Figures 10a and 10b.** Visual inspection of surface state of the embedded steel rebar. In order to avoid the phenolphthalein color change interfering with the appreciation of the images, the reinforcement steel was extracted before application of phenolphthalein to the specimen surface and put back in its place before the picture was taken.

#### 4. CONCLUSIONS

The ER application in partially carbonated specimens prepared with CPC and CPP, using  $K_2CO_3$  and  $Na_2CO_3$  as anolytes, allows us to conclude that:

- Under the experimental conditions of the technique, the pH recovery (realkalisation) on the concrete surface (8 mm of cover depth) is mainly obtained during the first 5 days, a period in which a higher increase in alkalinity is obtained. However, 13 days were needed to achieve complete realkalisation of initially carbonated concrete. This would imply less time for the current application compared to entirely carbonated concretes and with presence of steel reinforcement corrosion.
- The type of anolyte does not have a direct influence on the pH recovery in either type of concrete. In this case, the pH level reached on the zone close to the steel reinforcement and to the concrete surface is influenced by the type of cement used and the initial pH level of the concrete matrix.
- Measurements of the steel potential, even after depolarization of the system, do not suggest the actual thermodynamic state of the steel corrosion, as verified by the visual inspection of the surface state of the embedded steel rebar. The application of the electrical field, the introduction of

ions and the measurement conditions all change the chemical, electrochemical and dielectric properties of concrete, directly affecting the measurements and the resulting interpretation.

- Independently of the anolyte and the concrete type used, ER is unable to restore the pH to a value similar to that of non-carbonated concrete. However, the steady value or slight increment of pH together with the increment in the alkali content at the steel-concrete interface would support conditions that promote the stability of the steel passive layer. Therefore, electrochemical realkalisation can be applied as a preventive technique on partially carbonated concretes.

In summary, under the experimental conditions developed in this investigation, all the results lead to the conclusion that electrochemical realkalisation can be applied as a preventive technique in partially carbonated concrete. It should be mentioned that the proposed ER approach emphasizes the importance of a tradition of inspection and routine maintenance of structures (increasingly accepted and applied in civil engineering) in which a complete diagnosis of the structure should be developed in order to verify the viability of the application of ER and of other intervention techniques. Future works might be required to determine the application limits of ER as a method of preventing corrosion by concrete carbonation, i.e., specimens made with lower w/c ratios than those used in this work should be analyzed.

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