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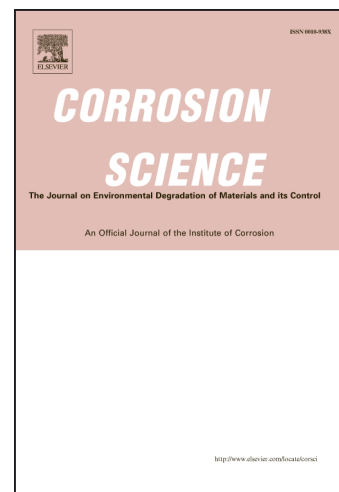
Efficiency of a conductive cement-based anodic system for the application of cathodic protection, cathodic prevention and electrochemical chloride extraction to control corrosion in reinforced concrete structures

J. Carmona, P. Garcés, M.A. Climent *

Civil Engineering Department, University of Alicante, PO Box 99, 03080 Alicante, Spain.
(*): Corresponding author. Phone: +34 96 5903707. E-mail address: ma.climent@ua.es

Abstract

This article describes the research carried out regarding the application of cathodic protection (CP) and cathodic prevention (CPrev), in some cases with a pre-treatment of electrochemical chloride extraction (ECE), on representative specimens of reinforced concrete structures, using an anodic system consisting of a graphite-cement paste applied as a coating on the surface. The aim of this research is to find out the competence of this anode for the aforementioned electrochemical treatments. The efficiency of this anode has been clearly demonstrated, as well as its capability to apply a combined process of ECE and after CP.

Keywords: A. Steel reinforced concrete; Graphite-cement paste; B. Galvanostatic; Electrochemical chloride extraction; C. Cathodic protection.

1. Introduction

The main enemy of the durability of concrete structures is the corrosion of steel reinforcement, and this effect is chiefly caused by penetration of chlorides (Cl^-) in the concrete mass. Since the last quarter of the past century researchers have been developing electrochemical treatments aimed at preventing the penetration of chlorides in concrete and to remedy its effects. Some patents have been registered and its techniques have been applied to many infrastructure works with good results, as a rule. Therefore, it is generally accepted that both cathodic protection (CP) and electrochemical chloride extraction (ECE) are appropriate and efficient methods to improve the durability of reinforced concrete structures [1-5].

The mechanism of CP in order to restore the lost protection condition to the corroded steel is known. It consists essentially in the transformation of the environment around the rebars, removing Cl^- and generating OH^- at its surface as was shown by Glass and Chadwick [6]. This can be long-lasting effect as was demonstrated by Christodoulou et al. [7].

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Following Pedeferri and coworkers [8-9], two different sorts of applications can be distinguished for CP by impressed current. In one hand, cathodic prevention (CPrev), which aims to protect non corroding reinforced concrete structures against the onset of corrosion by chlorides, by using low cathodic current densities in the range of 0.5-2 mA/m^2, which increase the critical chloride content for pitting corrosion of steel. On the other hand, cathodic protection (CP) strictly speaking, which is known to aim to stop corrosion in constructions where the process caused by the action of chloride is already happening. These latter CP applications usually are run with higher cathodic current densities of up to 15 mA/m^2 or 20 mA/m^2.

With this research the behavior of a cement-based anode system for the application of both electrochemical techniques (ECE and CP) is discussed. A new generation of modified materials are allowing this kind of applications. This type of materials, able to simultaneously offer different properties in the systems where they are used, are known as "multi-functional" [10-15]. Among them, conductive pastes and mortars have recently opened a new field to design anode systems for electrochemical techniques. The first steps on this path were the development of anodic systems for CP, as reflected in researches of Fu and Chung [16], Hou and Chung [17], DePeuter and Lazzari [18] and Bertolini et al. [19]. As for ECE, also new coatings as mortars and pastes have been developed to form anodic systems using carbonaceous conductive materials. Following this line, the purpose of this paper is to focus on the graphite-cement pastes, as a continuity of previous researches of Pérez et al. [20] and Cañón et al. [21]. The new contribution of this research consists in the use of an anode to apply CP and CPrev, as well as to combine treatments ECE-CP or ECE-CPrev. The solution of using a paste instead of a mortar provides, a priori, several advantages. Its thickness (2 mm) is about ten times thinner than a mortar, avoiding the addition of dead load to treated structures. Furthermore, both manufacturing and application processes are price competitive. Besides, its ability to retain moisture facilitates the maintenance of the electrolyte on the surface [21]. But above all, the best of its powers is to make the implementation of ECE and CP successively feasible. This capacity is essential to apply ECE before CP treatment in structures with a large Cl$^-$ contamination, and exposed to an aggressive environment that makes likely a new increase of the Cl$^-$ content of concrete after the ECE treatment. It must be recalled that the current density needed for a successful CP treatment is higher the higher is the Cl$^-$ content of concrete [8]. Up to our knowledge, there is no previous publication testing an anodic system in regard to this dual efficiency, for ECE and subsequent CP.

In short, the objectives of this research can be classified into three groups:
1. Obtaining complementary data about the efficiency and results of an anode system composed of a paste of graphite-cement overlay for ECE application on reinforced concrete.

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2. Checking the efficiency and feasibility of an anode system composed of a paste of graphite-cement overlay for CP and CPrev applications on reinforced concrete.

3. Verifying the possibility of using the same anodic system for a combined treatment of ECE+CP on reinforced concrete.

2. Experimental procedure

2.1. Materials used

Samples are designed to be treated with ECE, CP and CPrev. For ECE and CP, samples of concrete were manufactured with 2% Cl^- related to mass of cement, by adding NaCl in the mixing water. The intention is to assure a content of Cl^- that clearly exceeds the critical chloride threshold in order to depassivate the steel, as was stated by Angst et al. [22-23]. The rest of the concrete dosage was 250 kg/m³ of Portland cement CEM I 42.5 R, water-to-cement ratio of 0.65, 2.50 kg/m³ of superplasticizer, and 1,890 kg/m³ of aggregate with maximum size 12 mm. Thus, a concrete of compressive strength 37.8 N/mm², porosity 11.1% and bulk density 2,380 kg/m³ was obtained. For CPrev application, the concrete had the same dosage but without Cl^-. The dimension of the specimens was 18 x 18 x 8 cm³, which were reinforced by a grid 16 x 16 cm² composed of six steel bars soldered symmetrically forming squares of 5 cm side, and placed 2 cm under the anode.

Two copper connectors isolated by plastic were screwed to the rebar, to connect them with the negative pole of the electric source, composing the cathode system, Fig.1. Design criteria for the reinforcement arrangement were inspired by experiences of Garcés et al. [24-25].

Once the formwork was removed, specimens were moist-cured at 95-98% relative humidity (*RH*) for 28 days. To form the anode system, a graphite-cement paste was prepared by mixing graphite powder and Portland cement at 50%-50% in mass. Water to solid mix ratio was 0.8. Secondly, a 2 mm thick layer of this paste was applied on the surface of each specimen, and then all of them were moist-cured for 10 days. After that, two grooves were performed lengthwise onto the anodic overlay, without reaching the concrete surface, in order to receive both graphite rods to connect to the positive pole of the electric source. To finish up, these rods were overlaid with graphite-cement paste in order to join with the anode system perfectly, but avoiding any contact between graphite rods and concrete. A PVC receptacle was assembled on the top of the samples to retain both ECE electrolyte (distilled water) and/or the dissolution used during CP or CPrev applications to simulate a continued chloride contamination (65 ml NaCl 0.5 M applied weekly), Fig. 2. The ratio between the surface of concrete covered by the anodic overlay and the surface of the primary anodes (graphite rods) was 9.6; the ratio between the surface of concrete covered by the anodic overlay and the total surface of the steel bars was 1.7, Fig. 2. All current density and electric charge density values reported in this work are relative to surface of concrete, (equal to the anode surface), except otherwise stated.

The resistivity of the graphite-cement paste was measured through the four-probe method. To this end paste specimens were cast in 4 x 4 x 16 cm³ molds, and moist-cured at 95-98% *RH* during 14 days. The experimental details of the measurements can be found elsewhere [26]. The average obtained resistivity was 1.5 Ω m.

The measurements of steel corrosion potential (E_{corr}) and all the single electrode potentials, were performed using Ag-AgCl reference electrodes. These electrodes were housed in respective holes drilled from the exposed surface of the concrete specimen (that bearing the graphite-cement anode) to the vicinity of the rebar. For this purpose, the holes were sheathed with a plastic tube, and filled with a KOH 0.2 M dissolution, Fig. 2.

In this way nine specimens were prepared, seven of them with salt in the mixing water and two without it. Two of the salted specimens were used only for determining the efficiency of the ECE process (section 2.2.1), i.e. concrete cores were extracted from them, and their chloride content profiles were determined, in one case before and in the other case after ECE. These two specimens were discarded after coring. The seven remaining specimens were intended for the tests corresponding to CP, Cprev, and the combined treatments (ECE+CP) and (ECE+CPrev), see section 2.2.2.

2.2. Case studies carried out

2.2.1. Case study 1: Application of ECE

Initially four of the specimens made with saline mixing water were subjected to ECE. For this purpose, the specimens were electrically connected in series by pairs to a direct current source. The relevant parameters of the ECE treatments are shown in Table 1. A low charge density was applied, only 1.5 MC/m² relative to concrete surface (2.6 MC/m² relative to steel surface). The current source feeding voltage (ΔE_{feed}) was controlled at a level below 40 V during the processes, for safety reasons. It was necessary in this respect to interrupt the current passage two times (pauses 1 and 2 of 24 h) along the treatment. As an example, the evolution of ΔE_{feed} during the second half of an ECE process is shown in Fig. 3, for two of the ECE treated specimens.

The whole processes were performed inside a fume hood to eliminate the chlorine, $Cl_2(g)$, produced by electrochemical oxidation of the Cl⁻ ions extracted from the concrete.

When the ECE processes were finished, pH values of the electrolytes were measured in order to check the acidifying effect caused by the electrochemical anodic reactions.

The next step was to obtain the Cl⁻ content profiles of concrete cover on steel, both before and after ECE. For that purpose a concrete core was extracted from one of the specimens with salt in the mixing water but not subjected to ECE; and another core from one of the ECE treated specimens, using a 7 cm diameter drill. The extracted cores were subjected to a grinding process, [27], to get concrete dust samples corresponding to thin (2 mm thick) successive

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parallel layers to the exposed surface. Thus, 10 dust samples were extracted from the 2 cm concrete cover. The measurement of the samples acid-soluble Cl⁻ contents was carried out by potentiometric titration as stated by Climent et al. [28-29]. These values are always expressed as percentage relative to mass of cement in concrete. The local and overall efficiencies of the ECE treatments were calculated with the Cl⁻ contents before and after ECE [30-31].

The three remaining ECE treated specimens were kept for the further combined treatments ECE+CP and ECE+Cprev.

2.2.2. Case study 2: Application of CP, CPrev and the combined treatments ECE+CP and ECE+CPrev

The purpose of this study was to investigate the possibility of using the graphite-cement overlay anode for applying protective treatments of CP, CPrev, ECE+CP and ECE+CPrev, to laboratory model reinforced concrete specimens [32]. Table 2 establishes the adopted nomenclature of the specimens and the electrochemical treatments applied to each one. It must be stressed that all specimens included in Table 2, even those that were not given any of the electrochemical treatments (R and P), were subjected to the same salting regime during the 24 weeks period that lasted the CP or CPrev treatments: 65 ml NaCl 0.5 M weekly sprayed onto the concrete or anodic overlay surface, in order to simulate continued chloride contamination.

The CP treatments were applied with 15 mA/m² of current density (relative to concrete or anode surface) to two specimens, one of those previously treated with ECE (EA in Table 2) and the other one without previous treatment (A in Table 2). On the other hand the application of CPrev with 2 mA/m² of current density (relative to concrete surface) to a sample previously ECE treated (EB in Table 2) and to another manufactured without salt and not ECE treated (B in Table 2). The values of the current densities relative to the steel bars surface are 25.5 mA/m² and 3.4 mA/m² for the CP and Cprev treatments, respectively. Each application has its reference sample without treatment of CP or CPrev to compare the results. The reference sample for the specimens subjected to combined treatments (EA for ECE+CP, and EB for ECE+CPrev) is ER. R is the reference for A, and P is the reference for B.

The application of CP and CPrev consisted of two phases.

Phase 1. First 24 weeks. The aforementioned treatments CP and CPrev were continuously applied during the first 13 weeks. Then, the current was switched off for 4 weeks and after that treatments were resumed to the end. Chloride contamination was continuously applied, even during the switch off periods.

While applying the CP and CPrev treatments some parameters representative of the corrosion state of steel were measured in open-circuit conditions. During the two first weeks, the steel corrosion potential (E_{corr}) was daily measured by means of an Ag-AgCl reference electrode. Since the third week both the corrosion potential and the steel corrosion rate i_{corr}

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(μA/cm²) were determined weekly. The i_{corr} measurements were taken with a Gecor6 device (Geocisa, Madrid, Spain). Gecor6 is a portable measurement unit based on the linear polarization resistance method. The equipment uses a modulation confinement technique, allowing the quantitative determination of the corrosion rate [33]. During the current passing periods the feeding voltage of each specimen, ΔE_{feed}, was obtained as the potential difference between cathode and anode; and the individual anodic and cathodic potentials, E_a and E_c, respectively, were measured against the reference electrode Ag-AgCl. Finally, in order to check the efficiency of CP and CPrev as maintainers of protection conditions of steel, the "100 mV decay" criterion was used, as is specified in ISO 12696:2012 [34]. This criterion has been also extensively employed for this purpose by several researchers as Bertolini et al. [19] and Glass et al. [35]. The method consists in obtaining the 4 hour potential decay (ΔE_{decay}), that is the difference between E_c^{4h} (the value of E_c 4 hours after the current switch off), and the instant-off cathodic potential E_c^{io}, which in this case was measured 1 s after the current switch off. The minimum value of the 4 hour depolarization must be 100 mV for an adequate corrosion protection of steel [34]. The values of E_c^{io} were monitored with an automatic data logger able to obtain and record 500 measurements in 6 seconds, after the current switch off.

Once the 24 weeks processes were fulfilled, cores were extracted from all specimens of Table 2, and their respective Cl⁻ content profiles were obtained.

Phase 2. At the end of Phase 1 it was observed that all the specimens had lost the steel protection condition, evidenced by ΔE_{decay} values lower than 100 mV. Then, it was decided to start this second phase with the objective of recovering the protection conditions of steel by adjusting the current density of the CP treatments. The procedure was to increase progressively the current density during 4 weeks, starting with a value of 20 mA/m², until obtaining the protection conditions.

3. Results and discussion

3.1. Application of ECE

Fig. 3 shows the evolution of the ΔE_{feed} values during the final part of the ECE treatment applied to two of the reinforced concrete specimens. It is appreciable a progressive increase of ΔE_{feed} with time. The origin of this evolution can be due to an increase of the electric resistivity of concrete, which in turn can be brought by modifications of the composition of the inner concrete electrolyte and the microstructure of the concrete porous network during the application of electric fields. These modifications have been observed during ECE [36] or ionic migration [37] experiments. The voltage increase can be also partially due to electrode polarization effects.

Once finished the ECE process with the settled parameters, Cl⁻ content profiles were obtained, corresponding to the states before and after the ECE treatment, see section 2.2.1. The

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local ECE efficiencies, understood as percentage of Cl⁻ content removed, are plotted in Fig. 4. The average of removed Cl⁻ was 51% of the initial content. This indicates a good performance of the ECE process applied on a conventional ordinary Portland cement concrete with the anodic conductive overlay system, for a relatively low charge density of 1.5×10^6 C/m² relative to concrete surface. This result can be compared to the 41% efficiency obtained for a very similar reinforced concrete element, with the same initial amount of Cl⁻, subject to an ECE treatment, using a Ti–RuO₂ mesh anode, and passing a total charge density of 1 MC/m² relative to concrete surface [20].

The pH values determined for the electrolytes, after the ECE experiments, were in the range 5-5.5. This means that the acidity of the electrolytes has increased slightly, (the initial electrolyte was distilled water). This acidifying effect may be due to several of the electrochemical anodic reactions, namely the oxidation of hydroxide ions or water to O_2(g) and the oxidation of carbon to CO_2(g). It is possible that the alkaline character of the graphite-cement paste anode may have reduced the acidity produced by those electrochemical processes.

Another interesting feature, which is evidenced by the research, is the higher resistance to further Cl⁻ penetration of the elements treated with ECE, for a given level of external Cl⁻ load. Table 3 shows the evolution of local Cl⁻ contents for the specimens R (not treated with ECE) and ER (ECE treated), during the posterior Cl⁻ contamination. It is recalled that Cl⁻ contamination consists of 24, once per week, spray applications of 65 ml of NaCl 0.5 M, see Section 2.1. The sample treated with ECE experienced a reduction of the capacity of Cl⁻ absorption, during the 24 weeks of contamination, 17.4% lower, in average, than the not treated one, see Table 3. This may be due to the modification of the pore network of concrete caused by the action of the ECE treatment [36].

3.2 Application of CP, CPrev and the combined treatments ECE+CP and ECE+CPrev

Figs. 5 and 6 show the evolutions of the open-circuit E_{corr} values for the specimens of Table 2 during the duration of the first phase of the CP or CPrev experiments (24 weeks). In a similar manner Figs. 7 and 8 show the evolutions of the i_{corr} values for the same specimens. It must be recalled that, during the 24 weeks treatments, all specimens were subjected to an intense chloride loading regime, see Section 2.2.2.

For the three specimens previously treated with ECE, Fig. 5 shows that the initial E_{corr} values were equal or higher than -100 mV, typical values of steel corrosion potentials after ECE [2]. The E_{corr} values of EB (ECE+Cprev) quickly fell to values below -400 mV; the EA specimen (ECE+CP) kept during 6 weeks values about -100 mV, finally falling below -400 mV after 10 weeks; and the reference specimen ER (only treated with ECE) showed an intermediate behavior with an initial falling to values of about -200 mV, finally reaching values below -400 mV after 11 weeks. It seems that a CP treatment with current density of 15 mA/m² (EA) was

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able to maintain protective conditions for steel during about 10 weeks despite the high chloride loading. On the other hand the CPrev treatment of 2 mA/m^2 (EB) was not able to provide protective conditions. This latter fact can be considered as expected since such low current density values are only effective for preventative treatments of reinforced concrete non previously contaminated with chlorides [8-9], while the three specimens of Fig. 5 started the 24 weeks trials with an initial Cl$^-$ content of about 1% (relative to cement mass), see Fig. 4.

The evolution of the E_{corr} values of the specimens non previously treated with ECE, Fig. 6, shows that in this case the CP treatment with 15 mA/m^2 current density (A) was not able to protect steel from corrosion, since the corrosion potential of steel in A reached values below -400 mV in two weeks, and its values was only slightly higher than those of the reference specimen non CP treated (R). This different behavior, when compared to the observations of the precedent paragraph, can be explained taking into account that the A and R specimens started the 24 weeks experiments with an initial Cl$^-$ content of 2% (relative to cement mass). To this we have to add the large progressive Cl$^-$ contamination due to the weekly salting regime. On the other hand the CPrev treatment with 2 mA/m^2 current density, given to the initially Cl$^-$ free specimen (B) allowed to maintain values of E_{corr} higher than -400 mV, and clearly higher than those corresponding to the reference specimen non CPrev treated (P), up to the interruption of the Cprev at 13th week. This is a further confirmation of the increase of the tolerance to chloride-induced corrosion for CPrev treated steel (current densities in the range 0.5 – 2 mA/m^2 of concrete surface). These low cathodic currents, applied from the beginning of the service life of a reinforced concrete structure, decrease the steel potential, so leading to important increases of the critical chloride content for pitting corrosion of steel [8-9].

From the observation of the evolutions of the steel corrosion rates during the 24 weeks treatments, Figs. 7 and 8, little difference appears between the behavior of the treated specimens (EA, EB, A, B) and their corresponding reference specimens (ER, R, P). Furthermore, in all cases i_{corr} values higher than 0.1-0.2 μA/cm^2 were obtained, which means that in no case a repassivation of steel was obtained in open-circuit conditions. A correct interpretation of these observations needs to consider that most of the tested specimens had experienced corrosion before starting the treatments, since the concrete was admixed with 2% Cl$^-$ relative to cement mass; and all the specimens were subject to a severe chloride load during the 24 weeks treatments. In these conditions it is practically impossible to obtain a permanent repassivation of steel with temporary electrochemical rehabilitation methods [38-39]; and even CP or CPrev treatments need to be continuously applied for maintaining the protective conditions for steel.

To verify the effectiveness of CP and CPrev treatments for protecting steel from corrosion, the "100 mV decay" criterion [34] was used, as stated in Section 2.2.2. Fig. 9 shows the evolution of the ΔE_{decay} values for all the specimens in Table 2, during the 24 weeks experiments. Regarding the EA specimen (ECE+CP), the protection conditions of steel were

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kept during 11 weeks because of cathodic current circulation, despite external Cl⁻ loading. On the other hand the ΔE_{decay} values of the A specimen (CP only) practically never reached the threshold value of 100 mV. These observations are in good agreement with the observed evolutions of the E_{corr} values, Figs. 5 and 6, and put in evidence that cathodic protection of 15 mA/m² current density (relative to concrete surface) is able to keep protective conditions for the steel reinforcement if the initial Cl⁻ content of the specimen is about 1% (EA). In the case of the specimen with initial Cl⁻ content of about 2% (A), a higher current density would be needed for reaching the protection conditions [8-9]. Regarding the CPrev treated specimens (cathodic current density 2 mA/m² relative to concrete surface), specimen B showed ΔE_{decay} values higher than 100 mV up to the current switch off at 13ᵗʰ week, confirming the capacity of continuously applied CPrev treatments to keep steel protection conditions for an initially Cl⁻ free reinforced concrete, despite extensive external Cl⁻ load [8-9]. On the other hand such a low current density is unable to protect steel if concrete is previously contaminated at a level of about 1% relative to cement mass, as shown for specimen EB (ECE+CPrev) in Fig. 9.

One of the limitations of surface applied anodes for ECE and CP is the acidification of the concrete in contact with the anode [19]. In this study, after finishing all the electrochemical treatments, the state of the anodic overlay and that of the primary anodes (the graphite rods) was observed visually, and no damage was apparent. The pH values of the electrolytes after ECE were in the range 5-5.5, indicating that the acidity of the electrolytes had increased only slightly, see Section 3.1. Another indication of absence of damage can be obtained by looking at the feeding voltage (ΔE_{feed}) values needed to maintain the current density values during the CP experiments, Fig. 10. Bertolini et al. [19] demonstrated that during CP treatments, if the conductive cement-based overlay was damaged due to acidity, the values of ΔE_{feed} showed a sharp important increase, with typical increases of about 3 V (for instance from values of 1-2 V to values of 4-5 V). Fig. 10 shows the evolution of ΔE_{feed} values for the EA specimen (treated by ECE+CP) and A specimen (treated only by CP). It is appreciable that the ΔE_{feed} values of EA are only about 0.2 V higher than those corresponding to A. If some damage or malfunction of the anode would be derived from the acidity produced during the ECE treatment, we should had observed a range of ΔE_{feed} values 2-3 V higher for the EA specimen than those corresponding to the A specimen. It is likely that the alkalinity of the anode, provided by the cementitious addition, may have avoided the possible damage due to acidity.

Pedeferri [8] stated that one of the beneficial secondary effects of CP was the "chloride barrier effect". The current circulation results in a reduction of the Cl⁻ on the rebar surface or in a reduction of the ingress of Cl⁻ into concrete. Tables 4 to 6 provide a further confirmation of this statement. These Tables show the local Cl⁻ contents and their variations during the 24 weeks treatments for the CP (Table 4), CPrev (Table 5), and the combined treatments ECE+CP and ECE+CPrev (Table 6). The last column of Table 4 contains the reductions of the chloride

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ingress due to CP action (specimen A), in comparison with the non CP treated specimen (R). The average reduction is 15.5%, reaching much greater values (39%-62%) in the vicinity of steel. CPrev also reduces the penetration of Cl⁻. Indeed, the sample subjected to CPrev (B) increased its Cl⁻ content 21.5% less than the corresponding not treated (reference sample P). See Table 5.

As regard the combined treatments, when CP and CPrev were applied after ECE, the partial barrier of Cl⁻ penetration operated as well, as is gathered in Table 6. Cl⁻ content in the ECE+CP treated specimen (EA) was in average 19.9% lower than in the specimen only subjected to ECE (ER). Practically the same difference occurred between EB (ECE + CPrev treated) and ER, 20.1 %, see Table 6.

Cl⁻ profiles after 24 weeks of treatment revealed other significant effects. The difference of the Cl⁻ profiles corresponding to EA and EB was negligible, Fig. 11. Therefore, it might be thought that the effects of corrosion protection could be similar. Nothing, however, could be further from the truth. Taking into account electrochemical controls (Fig. 9), it is clear that CP was able to achieve and keep the protection of steel for 11 weeks (specimen EA), whilst CPrev did neither for even one week (specimen EB). It seems that the effect of partial barrier against Cl⁻ penetration starts to operate at current densities of the order of CPrev, which is 2 mA/m² relative to concrete or anode surface. However, it does not imply that the cathodic protection effect is reached. As is known, this effect depends critically on the ionic Cl⁻/OH⁻ ratio reached, as stated by Pedeferri and Bertolini [4] and by Siegwart et al. [36]. For reinforced concrete contaminated with 1% Cl⁻ relative to cement mass, the CP effect is obtained for current densities of at least 15-20 mA/m² [4].

Given that after 24 weeks of treatments, including rest periods between the 13th and 17th weeks, the reinforcements had completely lost their protection conditions, and a CP of 15 mA/m² was unable to restore the protective conditions (Fig. 9), the second phase was started. The external Cl⁻ load was discontinued since all the specimens had reached very high Cl⁻ contents, see Tables 4-6. In these conditions CP was applied with higher current densities. The question was if it would be possible to recover the protection conditions of steel by increasing the current density to the appropriate value.

In the beginning of this last phase, current density was set at 20 mA/m². After 4 weeks in operation 100 mV of ΔE_{decay} was not reached, i.e. the protection conditions were not obtained, Fig. 12. Neither success was obtained in a second attempt with 25 mA/m² (data not shown in Fig. 12). Finally, a third step of 40 mA/m² was set. In this case, after 4 weeks, the rule of 100 mV of ΔE_{decay} was achieved for EA, A and B specimens. Moreover, protection conditions were verified with the measurement of depolarization potential difference values 7 days after switch off [34]. In fact, more than 150 mV of ΔE_{decay} was reached after 7 days (209 mV for EA, 211 mV for A and 153 mV for B). This efficiency of CP is similar to that obtained by Christodoulou

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et al. [7]. However, this was not the case for EB. After 4 weeks with the highest cathodic current density, the protection conditions were not recovered for this latter specimen.

To summarize, data of the most significant studies of the processes of CP and CPrev, with or without previous ECE, are collected in Table 7.

4. Conclusions.

An anodic system composed of a graphite-cement paste 50%-50% in mass with low thickness (2 mm) has shown comparable performances to other anodes more commonly used for the application of electrochemical treatments to reinforced concrete. In the light of the results of this research, the following aspects can be emphasized, namely:

1. Regarding the application of ECE, a substantial part of Cl⁻ was removed with a low applied charge density. Moreover, ECE applied in this way makes concrete more resistant to Cl⁻ penetration for a certain external load.

2. According to the results of CP, this electrochemical technique is able to provide protection conditions to steel, despite a severe internal and external chloride contamination, as long as the proper current density value is set, according to the Cl⁻ content present. Also, its capability to recover the lost protection conditions with the increase of current density was demonstrated.

3. Continuously applied CPrev with current density of 2 mA/m² is able to maintain a conventional concrete initially Cl⁻ free in protection conditions despite being exposed to a severe Cl⁻ load. However, it is unable to recover protection conditions if the initial Cl⁻ content is equal or higher than 1% relative to cement mass, subjected to the same experimental external chloride load.

4. CP and CPrev treatments are able to reduce the chloride ingress into reinforced concrete, in comparison with reference non treated specimens, thus providing further confirmation to the so called "chloride barrier effect".

5. The graphite-cement paste anode system makes possible to apply a combined treatment of ECE and then CP, only changing the current density in the electric source. No damage was observed in the anode after the whole combined process. This combination has shown to be capable of maintaing or recovering protection conditions if the cathodic current density is set to the appropriate value according to the Cl⁻ content present. This combined treatment also supposes a strong barrier to Cl⁻ penetration. Nevertheless, more research is needed to test these anodic systems in different conditions to fully ascertain their reliability for practical applications.

Acknowledgement

References

[1]. J. Tritthart. "Electrochemical Chloride Removal: An Overview and Scientific Aspects". The American Ceramic Society. (1998) 401-441.

[2]. J. Mietz. "Electrochemical Rehabilitation Methods for Reinforced Concrete Structures. A State of the Art Report". European Federation of Corrosion by the Institute of Materials. Book No 709. (1998).

[3]. C. Andrade, M. Castellote, C. Alonso. An overview of electrochemical realkalisation and chloride extraction, in: D.W.S. Ho, I. Godson, F. Collins, (Eds.), Proceedings of 2nd Int. RILEM/CSIRO/ACRA Conference on Rehabilitation of Structures, Melbourne, Australia, (1998) 1-12.

[4]. P. Pedeferri, L. Bertolini. "La durabilità del calcestruzzo armato", McGraw-Hill, Milano. ISBN 88 386 0845-8. 2000.

[5]. L. Bertolini, B. Elsener, P. Pedeferri, R. Polder "Corrosion of Steel in Concrete", Wiley-Vch. ISBN 978-3-527-30800-2. 2004.

[6]. G.K. Glass, J.R. Chadwick. "An investigation into the mechanisms of protection afforded by a cathodic current and the implications for advances in the field of cathodic protection". Corrosion Science. 36 (1994) 2193-2209.

[7]. C. Christodoulou, G. Glass, J. Webb, S. Austin, C. Goodier. "Assessing the long term benefits of impressed current cathodic protection". Corrosion Science. 52 (2010) 2671-2679.

[8]. P. Pedeferri. "Cathodic protection and cathodic prevention". Construction and Building Materials. 10 (5) (1996) 391-402.

[9]. L. Bertolini, F. Bolzoni, P. Pedeferri, L. Lazzari, T. Pastore. "Cathodic protection and cathodic prevention in concrete principles and applications". Journal of Applied Electrochemistry. 28 (12) (1998) 1321-1331.

[10]. D.D.L. Chung. "Electrically conductive cement-based materials". Advances in Cement Research. 16 (4) (2004) 167-176.

[11]. P. Garcés, J. Fraile, E. Vilaplana-Ortego, D. Cazorla, E. Gª Alcocel, L. Gª Andión. "Effects of carbon fibres on the mechanical properties and corrosion levels of reinforced Portland cement mortars". Cement and Concrete Research. 35 (2) (2005) 324-331.

12

[12]. P. Garcés, L. Gª Andion, I. De la Varga, G. Catalá, E. Zornoza. "Corrosion of Steel reinforcement in structural concrete with carbon material addition". Corrosion Science. Vol. 49 (6) (2007) 2557-2566.

[13]. E. Zornoza, G. Catalá, F. Jiménez, L. Gª. Andión, P. Garcés. "Electromagnetic interference shielding with Portland cement paste containing carbon materials and processes fly ash". Materiales de Construcción. 60 (300) (2010) 21-32.

[14]. P. Garcés, E. Zornoza, E.Gª. Alcocel, Ó. Galao, L.Gª. Andión. "Mechanical properties and corrosion of CAC mortars with carbon fibers". Construction and Building Materials. 34 (2012) 91-96.

[15]. H. Baoguo, Y. Xun, O. Jimping. "Multifunctional and smart carbon nanotube reinforced cement-based materials". Nanotechnology in Civil Infrastructure: a paradigm shift. (2011) 1-47.

[16]. X. Fu, D.D.L. Chung. "Carbon fiber reinforced mortar as an electrical contact material for cathodic protection". Cement and Concrete Research. 25 (4) (1995) 689-694.

[17]. J. Hou, D.D.L. Chung, Cathodic protection of steel reinforced concrete facilitated by using carbon fiber reinforced mortar or concrete, Cement and Concrete Research. 27 (5) (1997) 649–656.

[18]. F. DePeuter, L. Lazzari. "New conductive overlay for CP in concrete: results of long term testing". Corrosion/93, paper nº 325. NACE. Houston, 1993.

[19]. L. Bertolini, F. Bolzoni, T. Pastore, P. Pedeferri. "Effectiveness of a conductive cementitious mortar anode for cathodic protection of steel in concrete". Cement and Concrete Research. 34 (4) (2004) 681-694.

[20]. A. Pérez, M.A. Climent, P. Garcés. "Electrochemical extraction of chlorides from reinforced concrete using a conductive cement paste as the anode". Corrosion Science. 52 (2010) 1576-1581.

[21]. A. Cañón, P. Garcés, M.A. Climent, J. Carmona, E. Zornoza. "Feasibility of electrochemical chloride extraction from structural reinforced concrete using a sprayed conductive graphite powder-cement as anode", Corrosion Science. 77. (2013) 128-134.

[22]. U. Angst, B. Elsener, C. K. Larsen, Ø. Vennesland. "Critical chloride content in reinforced concrete – A review". Cement and Concrete Research. 39 (2009) 1122-1138.

[23]. U. Angst, B. Elsener, C. Larsen, Ø. Vennesland. "Chloride induced reinforcement corrosion: Electrochemical monitoring of initiation stage and chloride threshold values". Corrosion Science. 53 (2011) 1451-1464.

[24]. P. Garcés, M.J. Sánchez de Rojas, M.A. Climent. "Effect of the reinforcement bar arrangement on the efficiency of electrochemical chloride removal technique applied to the reinforced concrete structures". Corrosion Science, 48 (3) (2006) 531-545.

13

[25]. B. del Moral, Ó. Galao, C. Antón, M.A. Climent, P. Garcés. "Viabilidad de utilización de una pasta de cemento con nanofibras de carbono como ánodo en la extracción electroquímica de cloruros en hormigón" (Feasibility of using a cement paste with carbon nano-fibres as an anode for electrochemical chloride removal from concrete). Materiales de Construcción, 63 (309) (2013) 39-48.

[26]. O. Galao, F.J. Baeza, E. Zornoza, P. Garcés. "Strain and damage sensing properties on multifunctional cement composites with CNF". Cement and Concrete Composites. 46 (2014) 90-98.

[27]. Ø. Vennesland, M.A. Climent, C. Andrade. "Recommendation of RILEM TC 178-TMC: testing and modeling chloride penetration in concrete. Methods for obtaining dust samples by means of grinding concrete in order to determine the chloride concentration profile". Materials and Structures. 46 (3) (2013) 337-344.

[28]. M.A. Climent, E. Viqueira, G. de Vera, M.M. López. "Analysis of acid-soluble chloride in cement, mortar and concrete by potentiometric titration without filtration steps". Cement and Concrete Research. 29 (6) (1999) 893-898.

[29]. M.A. Climent, G. de Vera, E. Viqueira, M.M. López. "Generalization of the possibility of eliminating the filtration step in the determination of acid-soluble chloride content in cement and concrete by potentiometric titration", Cement and Concrete Research. 34 (12) (2004) 2291-2295.

[30]. M.A. Climent, M.J. Sánchez de Rojas, G. de Vera, P. Garcés. "Effect of type of anodic arrangements on efficiency of electrochemical chloride removal from concrete", ACI Materials Journal. 103 (4) (2006) 243–250.

[31]. M.J. Sánchez de Rojas, P. Garcés, M.A. Climent, "Electrochemical extraction of chlorides from reinforced concrete: variables affecting treatment efficiency". Materiales de Construcción, 56 (284) (2006) 17–26.

[32]. J. Carmona. "Pasta de grafito-cemento como ánodo en tratamientos electroquímicos contra la corrosión causada por cloruros en estructuras de hormigón armado" (Graphite-cement anode for electrochemical protective treatments against corrosion of reinforced concrete structures due to chlorides), PhD Thesis, University of Alicante, Alicante, Spain, 2014. (Only available in Spanish).

[33]. C. Andrade, C.Alonso, J. Gulikers, R. Polder, R. Cigna, Ø. Vennesland, M. Salta. "Test methods for on-site reinforcement corrosion rate measurement of steel reinforcement in concrete by means of the Polarization Resistance method. RILEM Recommendation of TC-154. Electrochemical Techniques for measuring metallic corrosion". Materials and Structures. 37 (2004) 623-643.

[34]. European Committee of Standardization CEN. Technical Committee CEN/TC 219. ISO 12696: 2012(en). "Cathodic protection of steel in concrete".

[35]. G.K. Glass, A. M. Hassanein, N.R. Buenfeld. "Cathodic protection afforded by an intermittent current applied to reinforced concrete". Corrosion Science. 43 (2001) 1111-1131.

[36]. M. Siegwart, J.F. Lyness, B.J. McFarland. "Change of pore size in concrete due to electrochemical chloride extraction and possible implications for the migration of ions". Cement and Concrete Research, 33 (2003) 1211-1221.

[37]. I. Sánchez, X.R. Nóvoa, G. de Vera, M.A. Climent. "Microstructural modifications in Portland cement concrete due to forced ionic migration tests. Study by impedance spectroscopy". Cement and Concrete Research, 38 (2008) 1015–1025.

[38]. J.M. Miranda, J.A. González, A. Cobo, E. Otero. "Several questions about electrochemical rehabilitation methods for reinforced concrete structures". Corrosion Science, 48 (2006) 2172-2188.

[39]. J.M. Miranda, A. Cobo, E. Otero, J.A. González. "Limitations and advantages of electrochemical chloride removal in corroded reinforced concrete structures". Cement and Concrete Research, 37 (2007) 596-603.

Figure captions

Figure 1. Sketch of reinforcement of samples and connection of cathodic system.

Figure 2. Sketch of specimen assembly.

Figure 3. Evolution of ΔE_{feed} during the final half of the ECE treatment (current density 2 A/m^2 of concrete exposed surface) for two of the specimens subject to ECE (named here as specimens 2 and 3). The specimens were electrically connected in series to the current source. Two pauses (interruptions of current passage during 24 h) were introduced to keep the maximum ΔE_{feed} values below 40 V for safety reasons.

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Figure 6. Evolution of E_{corr} during the CP and Cprev treatments, without previous ECE. A: CP; B: CPrev; R (2% Cl⁻ in the mix, not CP treated): reference specimen for A; P (no Cl⁻ in the mix, not CPrev treated): reference specimen for B. All of them subjected to Cl⁻ contamination during the 24 weeks. Current density values: CP: 15 mA/m^2, CPrev: 2 mA/m^2, both related to exposed concrete surface.

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Figure 12. Evolution of ΔE_{decay} during phase 2 of CP. First step of 4 weeks with 20 mA/m^2 of current density, and third step with 40 mA/m². Specimens A, B, EA and EB.

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Tables

ECE. Specimens with graphite-cement paste as anode. Electrolyte: dammed distilled water			
Initial %Cl⁻	2 % relative to cement mass		
Current density	2 A/m^2 of concrete exposed surface (3.4 A/m^2 of steel surface)		
Initial ΔE_{feed}	16-24 V	**Final ΔE_{feed}**	23-22 V
Electric charge density	1.5 MC/m^2 of concrete exposed surface (2.6 MC/m^2 of steel surface)		

Table1. Summary of ECE data

Studied techniques	CP	CPrev	ECE+CP	ECE+CPrev
Initial % Cl⁻ in concrete	2	0	2	2
Reference sample	R (no electrochemical treatment)	P (no electrochemical treatment)	ER (treated only with ECE)	
Treated samples	A (CP treated)	B (CPrev treated)	EA (ECE+CP treated)	EB (ECE+CPrev treated)

Table 2. Nomenclature of specimens for Case Study 2.

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Depth (mm)	Content of Cl⁻ in R before Cl⁻ contamination (24 weeks) (%Cl⁻)	Content of Cl⁻ in R after Cl⁻ contamination (24 weeks) (%Cl⁻)	Increase of Cl⁻ in R caused by Cl⁻ contamination ΔR (%Cl⁻)	Content of Cl⁻ in ER after ECE, before Cl⁻ contamination (24 weeks) (%Cl⁻)	Content of Cl⁻ in ER after ECE and Cl⁻ contamination (24 weeks) (%Cl⁻)	Increase of Cl⁻ in ER caused by Cl⁻ contamination ΔER (%Cl⁻)	Reduction of the capacity of Cl⁻ absorption due to the previous application of ECE (ΔR-ΔER)/ΔR (%)
0 - 2	0.295						
2 - 4	1.956	8.690	6.733	0.776	5.339	4.563	**32.2%**
4 - 6	1.934	7.966	6.032	0.924	5.612	4.688	**22.3%**
6 -8	1.816	6.851	5.035	0.821	5.286	4.465	**11.3%**
8 - 10	1.773	7.061	5.288	0.755	4.511	3.756	**29.0%**
10 - 12	1.899	5.006	3.107	0.981	3.722	2.741	**11.8%**
12 - 14	2.010	5.004	2.995	0.708	3.450	2.742	**8.5%**
14 - 16	1.953	4.827	2.875	1.264	3.753	2.489	**13.4%**
16 - 18	2.135	4.989	2.854	1.303	3.715	2.412	**15.5%**
18 - 20	2.298	4.345	2.047	1.204	2.989	1.785	**12.8%**
Average	**1.975**	**6.082**	**4.107**	**0.971**	**4.264**	**3.293**	**17.4%**

Table 3. Local Cl⁻ contents (expressed in % Cl⁻ relative to cement mass) and their variations during 24 weeks of Cl⁻ contamination. Last column shows the reductions of the capacity of Cl⁻ absorption due to previous ECE treatment.

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Depth (mm)	Content of Cl⁻ in A after CP and contamination (24 weeks) (%Cl⁻)	Content of Cl⁻ in R after contamination (24 weeks) (%Cl⁻)	Initial content of Cl⁻ in specimens R and A (%Cl⁻)	Increase of Cl⁻ in A after CP and contamination ΔA (%Cl⁻)	Increase of Cl⁻ in R after contamination ΔR (%Cl⁻)	Reduction of the increase of Cl⁻ content due to CP action (ΔR-ΔA)/ΔR (%)
0 - 2			0.295			
2 - 4	6.695	8.690	1.956	4.738	6.733	**29.6%**
4 - 6	5.659	7.966	1.934	3.724	6.032	**38.3%**
6 -8	6.246	6.851	1.816	4.430	5.035	**12.0%**
8 - 10	6.429	7.061	1.773	4.656	5.288	**12.0%**
10 - 12	6.260	5.006	1.899	4.361	3.107	**-40.4%**
12 - 14	5.511	5.004	2.010	3.501	2.995	**-16.9%**
14 - 16	4.722	4.827	1.953	2.769	2.875	**3.7%**
16 - 18	3.880	4.989	2.135	1.745	2.854	**38.9%**
18 - 20	3.067	4.345	2.298	0.769	2.047	**62.4%**
Average	**5.385**	**6.082**	**1.975**	**3.410**	**4.107**	**15.5%**

Table 4. Local Cl⁻ contents (% Cl⁻ relative to cement mass) and their variations during 24 weeks of Cl⁻ contamination. Last column shows the reductions of the increase of Cl⁻ due to CP action.

Depth (mm)	Content of Cl⁻ in B after CPrev and contamination (24 weeks) ($\%$Cl⁻)	Content of Cl⁻ in P after contamination (24 weeks) ($\%$Cl⁻)	Initial content of Cl⁻ in P and B specimens (without salt added in the mix) ($\%$Cl⁻)	Increase of Cl⁻ in B after CPrev and contamination ΔB ($\%$Cl⁻)	Increase of Cl⁻ in P after contamination ΔP ($\%$Cl⁻)	Reduction of the increase of Cl⁻ content due to CPrev action (ΔP-ΔB)/ΔP ($\%$)
0 - 2						
2 - 4	4.963	6.273	0.190	4.773	6.083	**21.5%**
4 - 6	4.733	5.746	0.229	4.504	5.517	**18.4%**
6 -8	4.799	5.372	0.240	4.559	5.132	**11.2%**
8 - 10	4.343	4.716	0.227	4.116	4.489	**8.3%**
10 - 12	4.002	4.656	0.212	3.790	4.444	**14.7%**
12 - 14	3.786	4.492	0.205	3.581	4.287	**16.5%**
14 - 16	3.273	4.753	0.199	3.074	4.554	**32.5%**
16 - 18	2.953	4.419	0.221	2.732	4.198	**34.9%**
18 - 20	2.615	3.933	0.227	2.388	3.706	**35.6%**
Average	**3.941**	**4.929**	**0.217**	**3.724**	**4.712**	**21.5%**

Table 5. Local Cl⁻ contents (expressed in % Cl⁻ relative to cement mass) and their variations during 24 weeks of Cl⁻ contamination. Last column shows the reductions of the increase of Cl⁻ content due to CPrev action.

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Depth (mm)	Content of Cl⁻ in EA after ECE, CP and contamination (%Cl⁻)	Content of Cl⁻ in EB after ECE, CPrev and contamination (%Cl⁻)	Content of Cl⁻ in ER after ECE and contamination (%Cl⁻)	Difference of increase of Cl⁻ (ER-EA)/ER (%)	Difference of increase of Cl⁻ (ER-EB)/ER (%)
0 - 2					
2 - 4	4.352	4.866	5.339	**18.5%**	**8.9%**
4 - 6	4.194	3.999	5.612	**25.3%**	**28.7%**
6 - 8	3.830	4.070	5.286	**27.5%**	**23.0%**
8 - 10	3.858	3.877	4.511	**14.5%**	**14.1%**
10 - 12	3.300	3.367	3.722	**11.3%**	**9.5%**
12 - 14	3.100	3.150	3.450	**10.2%**	**8.7%**
14 - 16	3.500	3.033	3.753	**6.8%**	**19.2%**
16 - 18	2.578	2.498	3.715	**30.6%**	**32.8%**
18 - 20	1.959	1.913	2.989	**34.5%**	**36.0%**
Averages	**3.408**	**3.419**	**4.264**	**19.9%**	**20.1%**

Table 6. Local Cl⁻ contents (expressed in % Cl⁻ relative to cement mass) after 24 weeks of Cl⁻ contamination for the ECE+CP treated specimen (EA), the ECE+CPrev treated specimen (EB) and the only ECE treated specimen (ER). Last two columns show the reductions of the increase of Cl⁻ content due to CP or CPrev actions, respectively.

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Specimens	Weeks till $E_{corr}<$ -400 mV Ag-AgCl	Weeks in passivation ($\Delta E_{decay}>$ 100 mV)	Reaction to current switch off	Final Cl⁻ content (% relative to cement mass)	Increase of Cl⁻ content (% relative to cement mass)	Protection is achieved at 40 mA/m²
EA	10	11	⬆⬇ $i_{corr}E_{corr}$	3.408	2.437	YES
EB	6	0	⬆⬇ $i_{corr}E_{corr}$	3.419	2.520	NO
ER	11	-	-	4.264	3.293	-
A	2	2	⬆⬇ $i_{corr}E_{corr}$	5.385	3.410	YES
R	6	-	-	6.082	4.107	-
B	16	13	⬆⬇ $i_{corr}E_{corr}$	3.941	3.724	YES
P	7	-	-	4.929	4.712	-

Table 7. Summary of results obtained from EA, EB, ER, A, R, B and P reinforced concrete specimens.

Figures
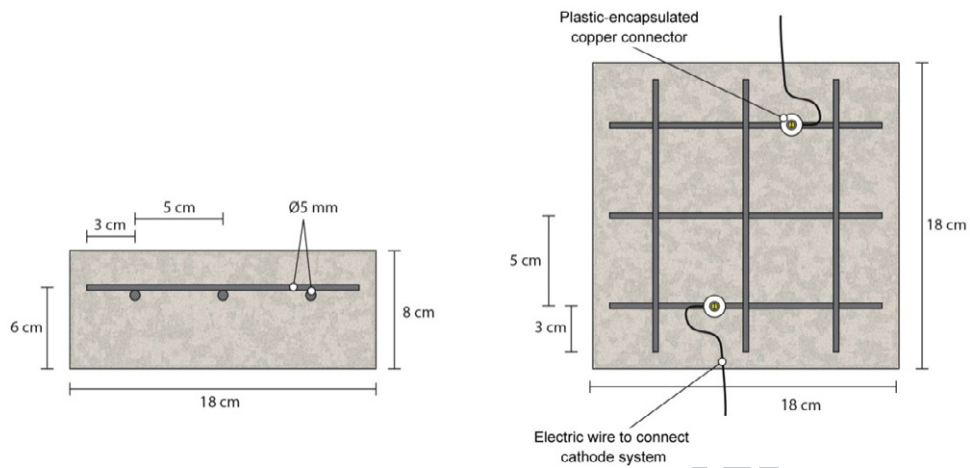
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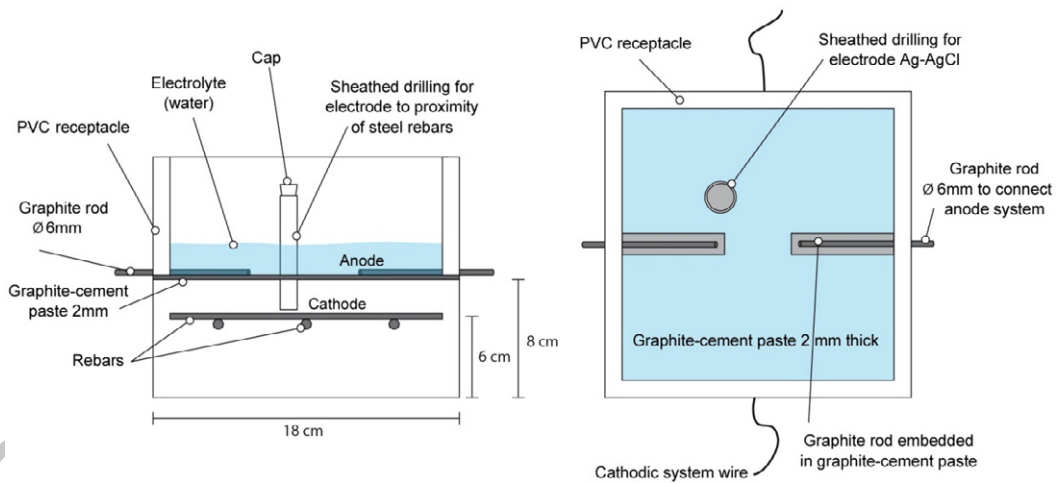
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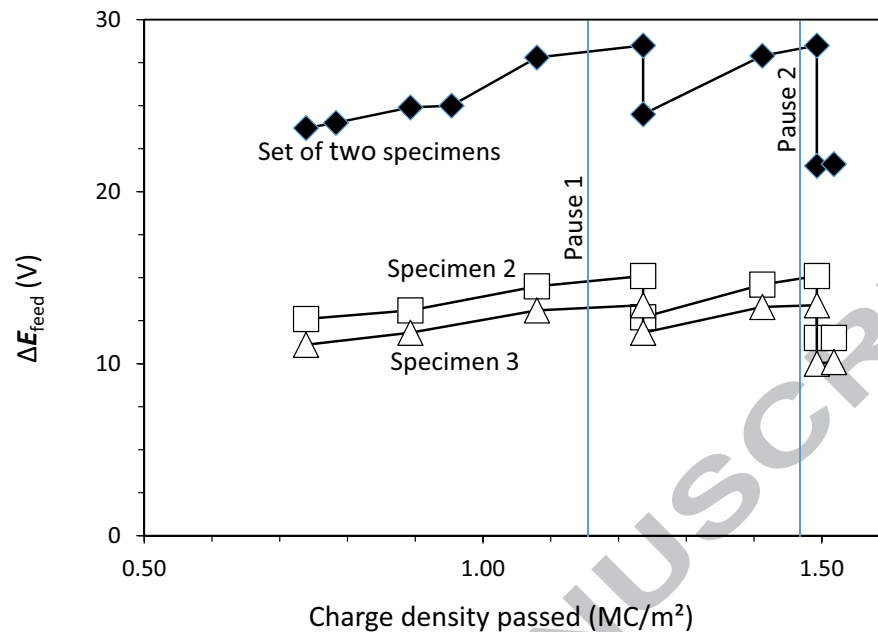
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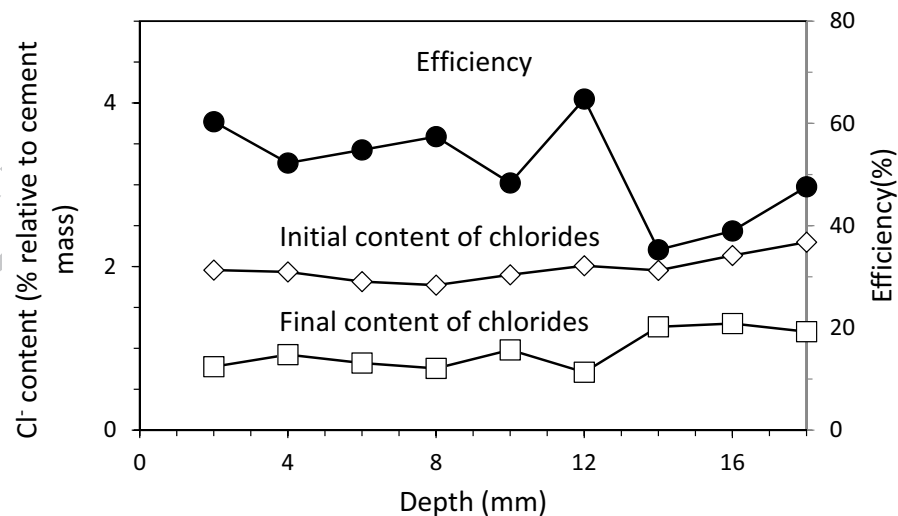
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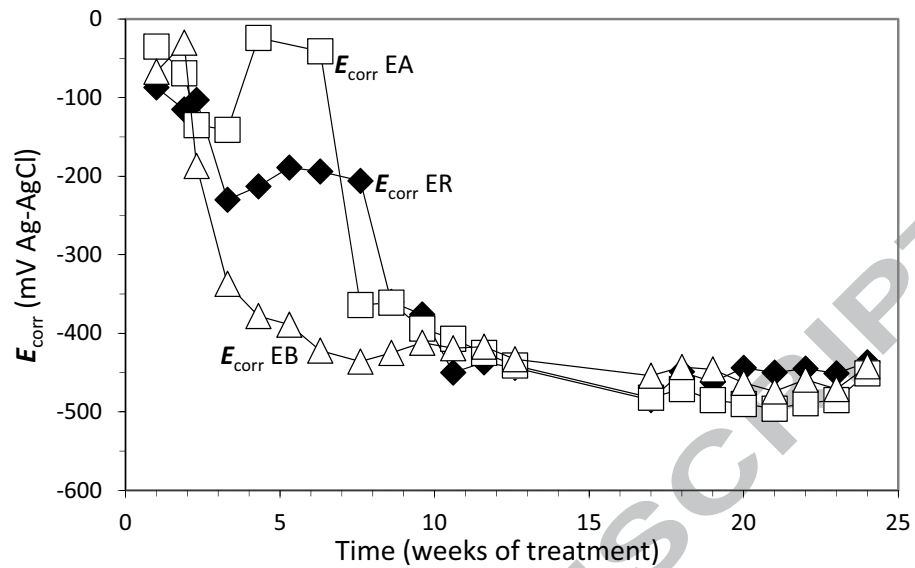
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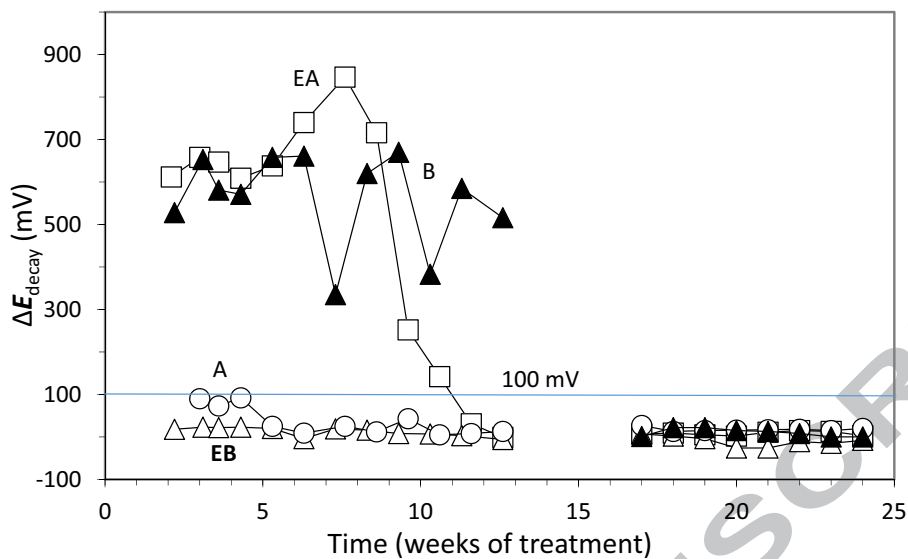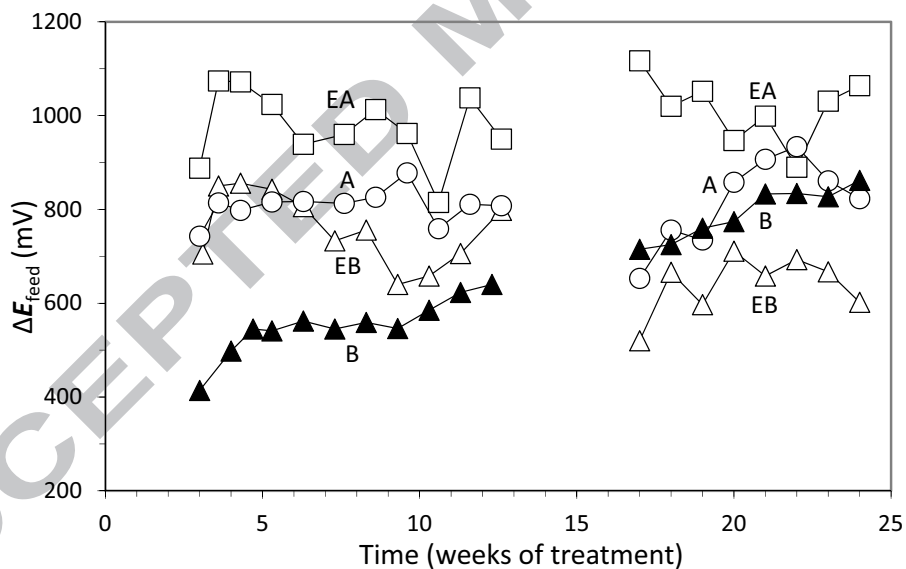

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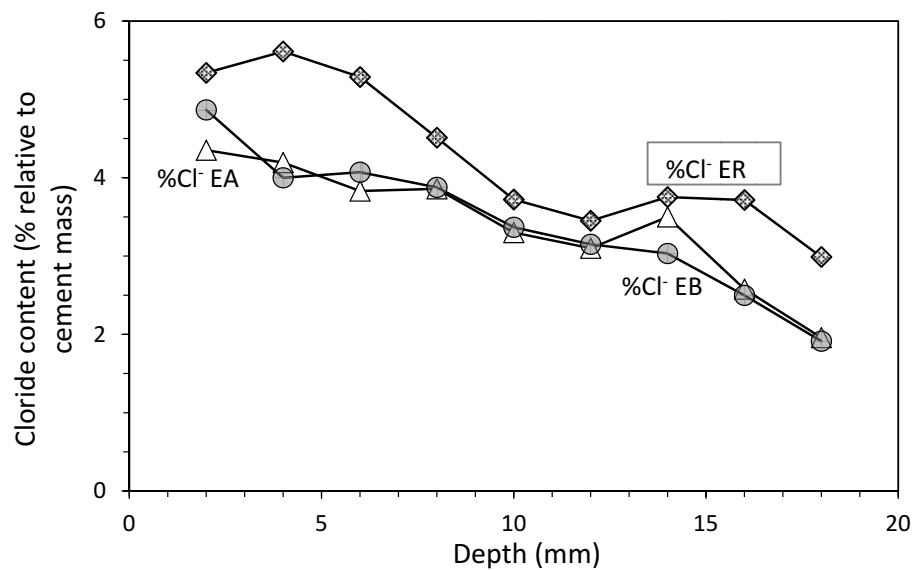
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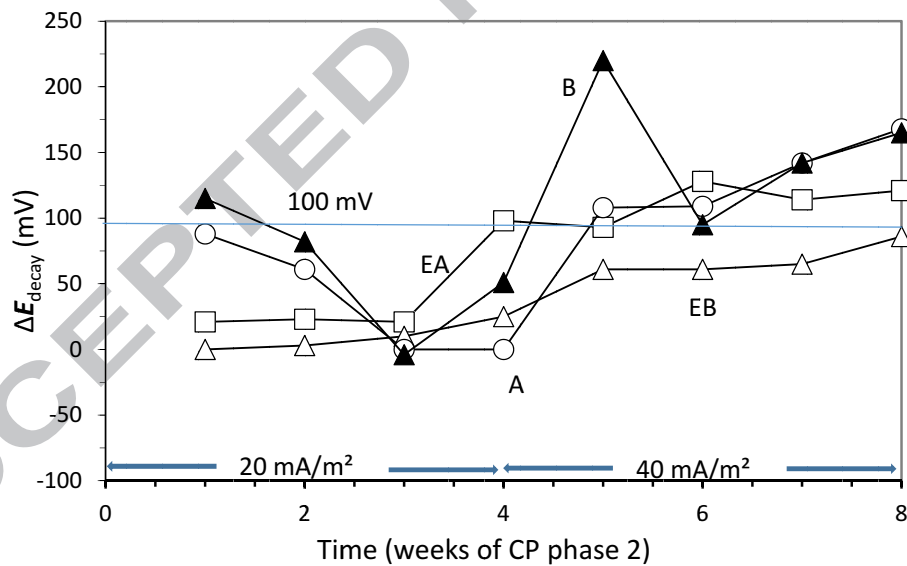
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Figure 12. Evolution of ΔE_{decay} during phase 2 of CP. First step of 4 weeks with 20 mA/m^2 of current density, and third step with 40 mA/m². Specimens A, B, EA and EB.

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Highlights

- Graphite-cement anode useful for low charge concrete electrochemical Cl⁻ extraction

- Electrochemical Cl⁻ extraction provides partial barrier against later Cl⁻ ingress

- Graphite-cement anode can be used for cathodic protection of reinforced concrete

- Graphite-cement anode useful for combined Cl⁻ extraction plus cathodic protection

- Combined Cl⁻ extraction-cathodic protection provide partial barrier to Cl⁻ ingress