Performance of carbon fiber added to anodes of conductive cement-graphite pastes used in electrochemical chloride extraction in concretes

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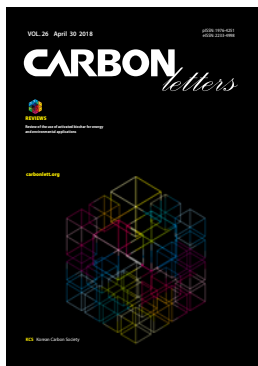
Abstract

Pollution of chloride ion-reinforced concrete can trigger active corrosion processes that reduce the useful life of structures. Multifunctional materials used as a counter-electrode by electrochemical techniques have been used to rehabilitate contaminated concrete. Cement-based pastes added to carbonaceous material, fibers or dust, have been used as an anode in the non-destructive Electrochemical Chloride Extraction (ECE) technique. We studied the performance of the addition of Carbon Fiber (CF) in a *cement-graphite powder* base paste used as an anode in ECE of concretes contaminated with chlorides from the preparation of the mixture. The experimental parameters were: 2.3% of free chlorides, 21 days of ECE application, a Carbon Fiber Volume Fraction (CFVF) of 0.1, 0.3, 0.6, 0.9%, a lithium borate alkaline electrolyte, a current density of 4.0 A / m^2 and a cement/graphite ratio of 1.0 for the paste. The efficiency of the ECE in the traditional technique using metal mesh as an anode was 77.6% and for CFVF of 0.9% it was 90.4%, with a tendency to increase to higher percentages of the CFVF in the conductive cement-graphite paste, keeping the pH stable and achieving a homogeneous ECE in the mass of the concrete contaminated with chlorides.

Key words: multifunctional material, corrosion current, graphite powder, concrete rehabilitation.

1. Introduction

In reinforced concretes, the arrival of the chlorides can break the passive layer, which triggers pitting corrosion [1]. Breaking the natural protection against corrosive agents causes active processes of corrosion that reduce the useful life of structures or exposed structural elements. To increase the useful life of damaged structures, the patching technique has been applied, consisting of removing damaged concrete due to the effects of corrosion, then cleaning the corrosion products and finally replacing the previously removed concrete. This type of repair has the disadvantage of generating zones in the concrete with different concentrations in its components, taking the structure to a state of risk. "Non -destructive" techniques have been developed in the last decades, such as the realcalization, the cathodic protection and the Electrochemical Chloride Extraction (ECE), in which the electrochemical properties of the materials are used to bring them to a state of protection or restoration. ECE is applied to concretes contaminated with chlorides, usually in a saline environment, where the

main purpose is to reduce the percentage of chlorides present in the cementitious mass to levels where chloride ions represent the lowest risk of producing corrosion. The application of ECE consists in generating for several weeks a current density at the surface of the concrete to be treated by an external electrode, titanium mesh or steel, impregnated with alkaline solution, to achieve steel surface densities higher than 4.0 A/m²; with this arrangement the electromigration of the chlorides is achieved towards the anode or external electrode [2].

On the other hand, concretes, mortars and cementitious pastes have low performance as electric conductors. In a dry state they are considered an insulating material and in wet state a low efficiency semiconductor. However, their conductivity properties can be modified by the addition of fibers or carbon base powders, leading them to be classified as semiconductors even in a dry state. The addition of carbon fibers dispersed in a cementitious matrix reaches the limit of electrical percolation in percentages much smaller than additions of graphite dust due to the high ratio aspect of the fibers. Even though the uniform dispersion of the fibers represents a problem, electrical contacts between the fibers are more efficient than in powders, which favor higher conductivity with lower percentages of addition. However, the low cost of carbon powders compared to fibers makes powders preferable to be used as an addition to concrete, mortars as in cementitious pastes. In addition to electrical properties, addition of carbon fibers also provides structural properties, giving rise to a multifunctional material of electrical and structural properties useful for simultaneous application [3-5].

The multifunctional material properties of cementitious materials with additions of carbon fiber or powders with electrochemical applications of cathodic protection in reinforced concretes, electrochemical extraction in concretes contaminated with chlorides, electrical percolation, double percolation, electrical conductivity and resistivity in cement base materials [6-14]. The application of cement-based conductive materials in electrochemical techniques originated in 1974 in the United States, where the cathodic protection system was installed in a vehicular bridge from an asphalt conductive layer: concrete: coke-crushed used as anode in the surface of the elements of reinforced concrete, and achieved acceptable efficiency results [15]. At present, multifunctional mortars have been used as anodes with the addition of graphite powder mechanically released to the surface of reinforced concrete elements contaminated with chlorides or with conducting cementitious pastes with additions of carbon fiber, achieving extraction efficiencies comparable to those obtained with the use of titanium mesh or stainless steel as an outer anode [6, 7, 16].

We evaluated the performance of a Conductive Cement Paste (CCP) base cement and graphite powder with different additions of carbon fiber as an anode in the application of the electrochemical extraction of chlorides in reinforced concrete structures contaminated with chloride ions.

2. Experimental

2.1. Materials

2.1.1. Reinforced Concrete Test Tubes with Chloride Content

ECE was applied to reinforced concrete tubes 28 days of age contaminated with 2.3% of chlorides in relation to the weight of the cement. The test tubes were cylindrical Ø7.0x14.0 cm reinforced with Ø3 / 8 "steel rods, designed according to the absolute volume method of the *Portland Cement Association* for the following parameters: a compressive design strength of 27.5 MPa, siliceous sand with a fineness modulus of 3.0, a maximum size of the thick aggregate of 12.7 mm and slump in a fresh state of 7.5 to 10.0 cm. After the tubes were cured, a layer of 10 ± 1 mm of CCP was applied to the lateral curved walls with a graphite bar at the center of its thickness for electrical contact. The application of ECE was performed after a period of 7 days of curing by immersion of the CCP in distilled water at 25 °C.

2.1.2. Conductive cement pastes

In the manufacture of the CCP mixtures, 30R type I Portland cement Composite was used with a water/cement ratio of 0.50, antifoam in 0.15% with respect to the weight of the cement and carbon fiber 10 mm in length, which is a common length used for reinforcement of cement pastes [17, 18]. The material dosage for the CCP was made according to Table 1, while the properties of the carbonaceous material are given in Table 2. The use of microsilica as an addition to the cementitious mixture guarantees the dispersion of the cement fiber in the matrix [19-21].

Table 1. CCP weight dosage

Paste Mix	Carbon Fiber*	Graphite powder / Cement	Microsilica / Cement
CCP-0.1	0.1		
CCP-0.3	0.3	1.0	0.15
CCP-0.6	0.6		

* Relation to the total volume of the mixture

Table 2. Properties of the carbonaceous material

Materials	Diameter (μm)	Superficial area (m²/gr)	Specific density
Carbon Fiber	10	0.227	1.76
Graphite Powder	-	2.29	1.85

2.2. Methods

2.2.1. Electrochemical extraction of chlorides

The external anodes used for the application of ECE were anodes considered inert: stainless steel mesh for the reference and PCC with a dosage according to Table 1 for the rest. In addition, lithium borate was used for an alkaline solution of 0.2 M, an accumulated load greater than 1500 A.h/m² and a current density in the steel surface of 4.0 A / m², as recommended by NACE SP0107-2007 [22] and with the purpose of reducing acidification and the generation of chlorine gas [23]. The periods of application of ECE were 8.0 and 21.5 days, corresponding to 768.0 and 2064.0 A.h/m². The experimental arrangement is shown in Fig. 1.
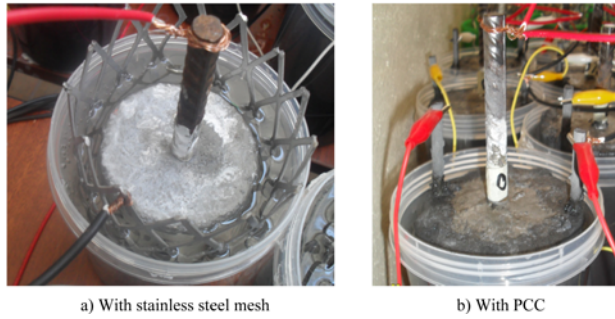
a) With stainless steel mesh   b) With PCC

Fig. 1. Experimental arrangement for ECE

Fig. 3. Micrography of CCP without CF, 50X

ganic Crystal Structure Database. There were no impurities of Fe, Zn or O due to grinding, which may affect the results of ECE application. Fig. 3 shows the dispersion achieved in the CCP. Addition of microsilica allowed an efficient dispersion, which achieved a uniform contact between grains of the graphite powder, which was advantageous for the electrical conductivity, even in a dry state.

3.1.2. Carbon fiber
Figures 4a) and 4b) show the dispersion achieved in the CCP with the addition of microsilica and antifoaming in the cement matrix. The dispersion achieved with the addition of microsilica enabled adequate contact of the carbon fibers with the graphite powder, creating the formation of a network that obtained conductivities appropriate for the use of the CCP as an anode in the aplication of ECE.

2.2.2. Percentage of free chlorides after ECE
The percentage of free chlorides was determined by chemical titration according to ASTM norm D1411-99, at 1.0 and 2.0 cm, of the reinforcing steel surface and in the middle part of the CCP to 8.0 and 21.0 days after the application of the ECE technique, and we verified the compliance of NACE SP0107-2007, which indicates as an acceptable limit 0.4% of free chlorides to one diameter of distance of the reinforcement [24]. In addition, weekly monitoring of the pH of the electrolyte and concrete was performed at the end of the ECE.

2.2.3. Monitoring of corrosion current densities (Icorr).
After ECE and a 30-day depolarization period, 7-day monitoring of Icorr was performed according to ASTM norm C-876-91 (re-approved in 1999) [25], using a standard calomel electrode (SCE).

3. Results and Discussion

3.1. Dispersion

3.1.1. Graphite powder
Fig. 2 shows the X-ray diffraction pattern of the graphite powder after mechanical grinding with steel spheres; it had the main signal of 2Θ at 25.70 and a secondary signal in 43.30, corresponding to the graphite according to the Inor-
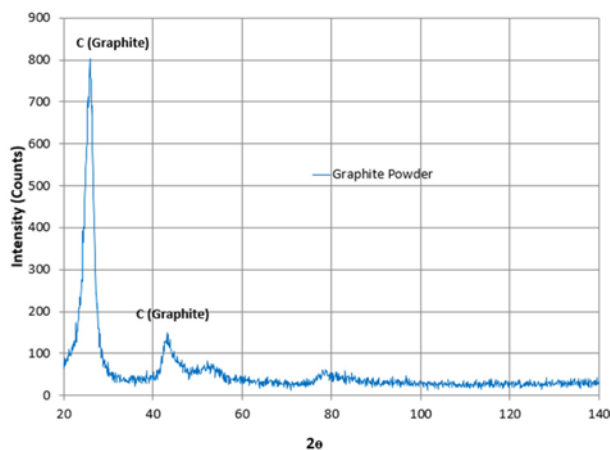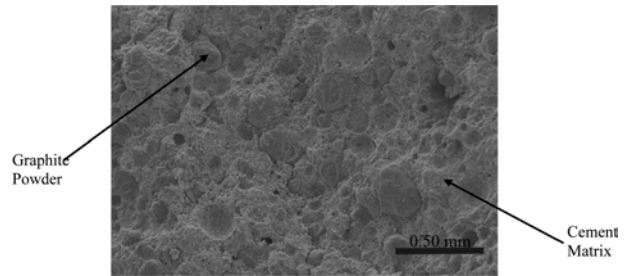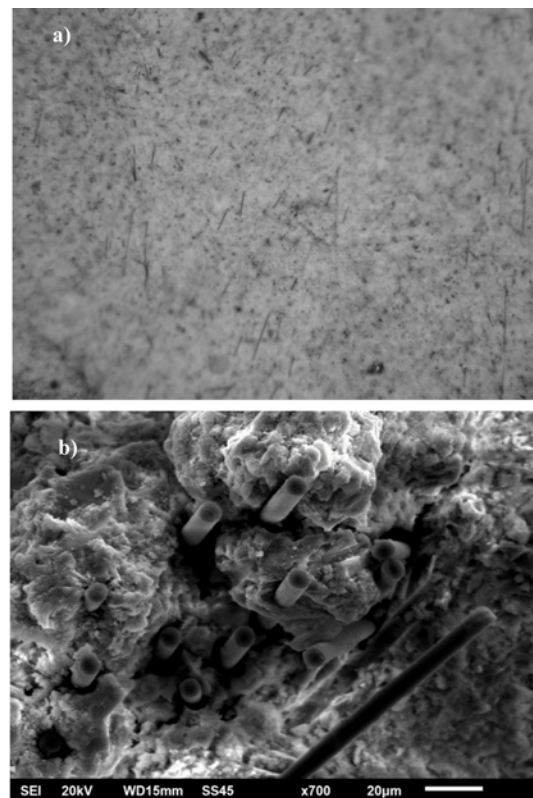

Fig. 2. X-ray diffraction pattern of graphite powder

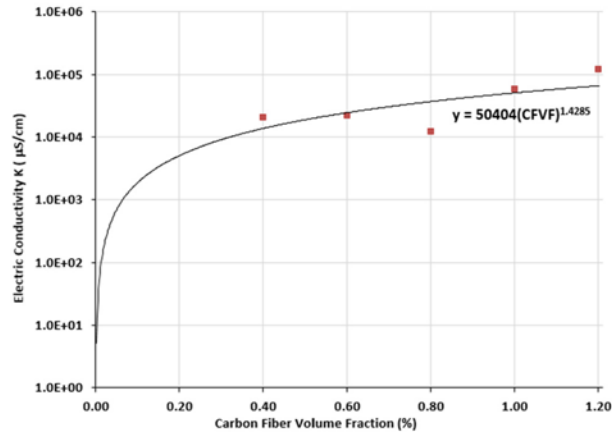**Fig. 4.** a) Photography and b) Micrography of CCP with CF

Fig. 5. Electrical conductivity of CCP

3.2. CCP Conductivity

Fig. 5 shows the electrical conductivity obtained in the CCP when Carbon Fiber (CF) was added in different volumetric fractions with respect to the total volume of the mixture. The electrical conductivity showed increases with the augmentation of CF with an exponential tendency, achieving an electrical conductivity of up to 119111.84 μS/cm for 1.2% of CF and always above the limit of electrical percolation of the material. However, mixtures with CF percentages above 0.60 had problems in their manufacture due to the low workability obtained by the high content of CF.

3.3. Preservation of the pH of the electrolyte

The application of ECE produces the acidification of the buffer solution of lithium borate, which must be able to maintain a stable pH as long as possible; here lies the success of the solution for this purpose. Fig. 6 shows the pH evolution of both the solution and the concrete at a distance of 1.0 cm of the reinforcing steel. The initial pH of the solution was 14.0 and decreased below 10.0 for CCP-0 and the reference, while for CCP-0.9 it was only below 11.0. The ECE generated the formation of water molecules and oxygen gas prior to the presence of OH- ions at the anodes, according to $2OH^- \rightarrow 1/2 O_2 + H_2O + 2e^-$. pH val-
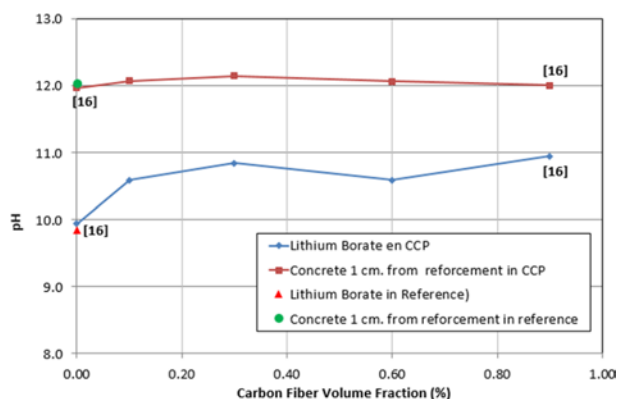
ues above 7.0 indicates that there was no evolution of chlorine gas in the course of ECE. On the other hand, the pH in the concrete remained in the order of 12.0, suggesting the passive state in the reinforcing steel embedded in the concrete contaminated with chlorides.

3.4. Chloride content in concrete and CCP

The natural process of diffusion of the chloride ions is towards the surface of the reinforcing steel. The application of ECE is intended to avoid the presence of the chlorides in the areas near the reinforcement and reduce the probability of triggering an active corrosion process. NACE SP0107-2007 recommendations [22] indicate as acceptable limit a value of 0.40% for the percentage of free chlorides with respect to the weight of the cement to a diameter of the surface of the steel. In investigations on ECE where inert metal anodes or conductive cementitious materials have been used, extractions of chlorides higher than 50 have been achieved [6-7, 16, 26-32]. Pérez *et al*., 2010 [6], with the use of a conductive cement paste with a weight ratio of cement: graphite: water of 1.0: 1.0: 1.0 as a counter-electrode and titanium mesh as an anode in ECE, exhibited chloride extractions of 65% and 41% of its initial content with currents of 5.0 and 1.0 A / m2 with respect to the steel surface, respectively. Additionally, A. Cañon *et al*., 2013 [7], with the use of a cement paste-aseptic graphite powder and a mesh of titanium, achieved efficiencies of 79% in both cases. The addition of carbon fiber to the conductive cement paste achieved decreases in the chloride content of up to 90.4% of free chlorides extracted for a volume fraction addition of carbon fiber of 0.9, compared to 77.6% in the traditional technique, which uses a stainless steel mesh as a counter-electrode. Fig. 7 shows the percentages of free chlorides obtained after the application of ECE in contaminated concretes at 1.0 cm of the surface of the reinforcement. The percentage of chlorides at the beginning of the ECE technique was 2.31%; at 8 days ECE values of 1.55, 1.58, 1.60, 1.66, 0.80 and 0.71% were obtained, while at 21 days 0.52, 0.47, 0.40, 0.53, 0.37 and 0.22% for
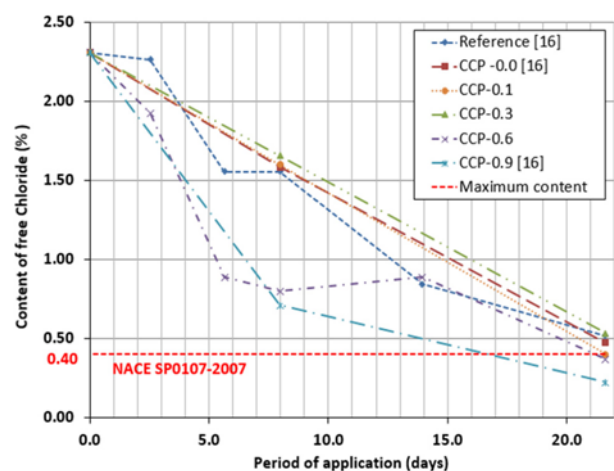

Fig. 7. Content of free chlorides to 1.0 cm from the surface of the reinforcing steel

Fig. 6. Variation of pH at 21 days of ECE

the traditional technique, and for conductive cement paste with 0.0, 0.1, 0.3, 0.6 and 0.9 for the Carbon Fiber Volume Fraction (CFVF), respectively. The maximum limit value was reached by the technique with conductive cement paste with a CFVF of 0.1, 0.6 and 0.9%, being the lowest one corresponding to a CFVF of 0.9. The CFVFs of 0.0, 0.1 and 0.3 had, in general, the same behavior as the reference, while CFVFs of 0.6 and 0.9 had the lowest percentage values of chlorides. The efficiency of these volumetric fractions of carbon fiber is due to their ability to retain a higher pH than the rest, even from the reference, for a current density of 4.0 A / m2 in the surface of the steel. In addition, CF provides a higher conductivity to the CCP, which increases the area of contact between the anode and the electrolyte, decreases the acidification of lithium borate and produces a homogeneous ECE in the mass of the concrete contaminated with chlorides.

Fig. 8 shows the percentages of free chlorides obtained after the application of ECE in concrete contaminated at 1.0 cm of the surface of the reinforcement. The recommendations of NACE SP0107-2007 [22] do not indicate maximum limit values of chloride percentages for this distance. The percentage of chlorides at the beginning of the ECE technique was of 2.31%; at 8 days ECE values were 1.32, 1.33, 1.39, 1.76, 0.89 and 1.32%, at 21 days 0.71, 0.68, 0.78, 0.53, 0.56 and 0.49% for the reference, CCP with 0.0, 0.1, 0.3, 0.6 and 0.9 in CFVF, respectively. CFVFs of 0.0 and 0.1 have, in general, the same behavior as the traditional technique, while CFVFs of 0.6 and 0.9 have the lowest percentage values of chlorides. The efficiency of the latter is due to its ability to retain a higher pH and a uniform current density.

Because the application of a CCP as an anode is a new technique in ECE, there is no minimum or maximum limit value in terms of its free chloride content. In applied techniques, the percentage of free chlorides in the CCP increased as the ECE progressed. Chlorides extracted from the concrete mass were retained in the mass of the CCP, which increased its percentage of chlorides. Fig. 9 shows the per-
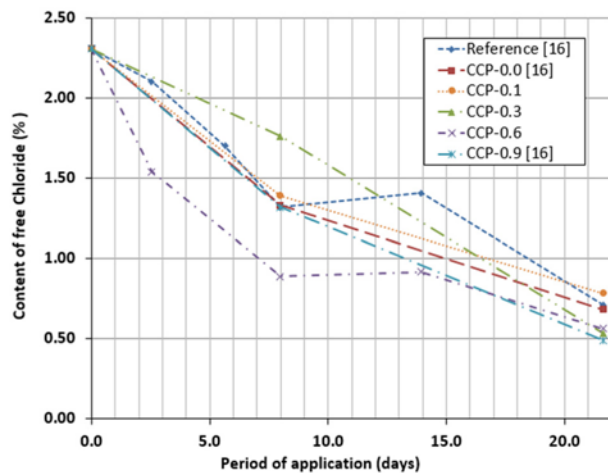
centage of free chlorides in the CCP, with values of up to 1.30% at 8 days of the ECE technique application and of 2.29% at 21 days, both the maximum values for a VF in CF of a CCP of 0.90. The percentage of chlorides in CCP at 8 days of ECE was 0.50, 1.09, 0.78, 0.81 and 1.30%, at 21 days 1.63, 1.63, 2.00, 2.16 and 2.29% for CCP with 0.0, 0.1, 0.3, 0.6 and 0.9 in their CFVF, respectively. CFVF values of 0.6 and 0.9 show the highest percentage values of chlorides, corresponding to the higher chloride extractions in the contaminated concrete. The capacity to contain more chlorides in the CCP in CFVF of 0.6 and 0.9 is due to the prevalence of a higher pH with respect to the rest of the CCP and the greater performance in the distribution of the density of load in the concrete surface.

Fig. 10 shows the ECE efficiency at 21 days of its application to contaminated concrete. In the reference, 77.6% was obtained and for a CFVF of 0.9% it was 90.4%. The efficiency trend was to increase to higher percentages of the CFVF in the CCP. The reference had a value comparable to the CFVF fraction in the CCP of 0.0%.
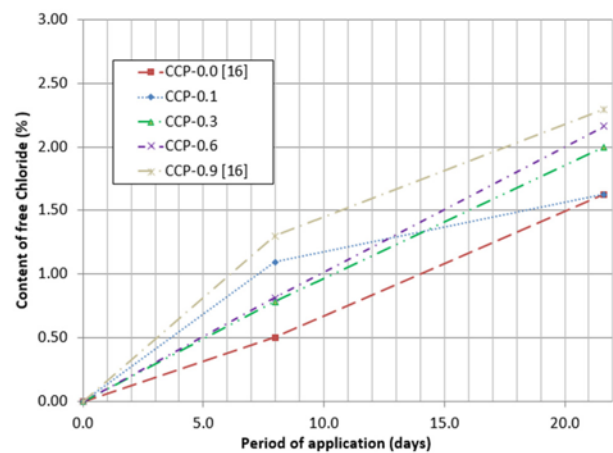

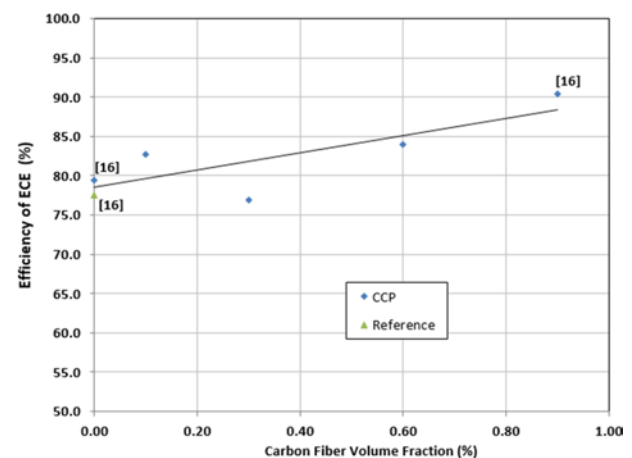**Fig. 9.** Content of free chlorides in CCP

Fig. 8. Content of free chlorides to 2.0 cm from the surface of the reinforcing steel.

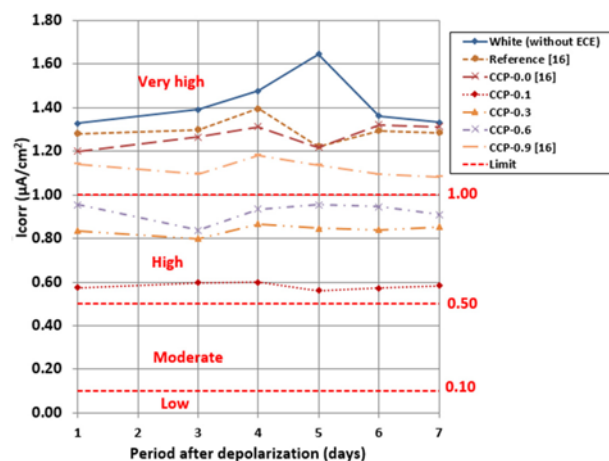**Fig. 10.** Efficiency of ECE at 21 days of ECE

Fig. 11. Icorr after depolarization with 21 days of ECE

3.5. Corrosion Current (Icorr) in concretes after ECE

The corrosion state of steel in reinforced concretes can be evaluated according to its Icorr according to the recommendations of the *Corrosion Manual, evaluation and diagnosis of corrosion in reinforced concrete structure* [33]. Fig. 11 shows the Icorr after ECE and a depolarization period; the percentages of decrement of the average Icorr with respect to the "blank" specimen without ECE were 8.8, 10.6, 59.1, 40.9, 35.1 and 21.1 for the reference and CFVFs in CCP of 0.0, 0.1, 0.3, 0.6 and 0.9, respectively. The lowest decrease was presented in the reference with 8.8% and the maximum in a CFVF of CCP of 0.1 with 59.1%. Although the ECE technique is not a technique for correcting corrosion but of eliminating its origin, with the addition of CF in the CCP, decreases in Icorr higher than the reference were obtained. This suggests that the addition in low volumetric fractions of carbon fiber in a conductive cement paste used in ECE has yields in the decreasing of Icorr more effective than a traditional technique and that the same paste of conductive cement for high values of VF.

4. Conclusions

The performance of the carbon fiber added to a conductive paste base cement and graphite powder used as an anode in the application of ECE was directly proportional to the VF of CF contained in the CCP due to the increase in the electrical conductivity of the CCP and the distribution of the current achieved on the surface of the contaminated concrete. The ECE efficiency trend was to increase with the augmentation of the CFVF contained in the CCP, achieving up to 90.4% of ECE for 0.9% VF of CF in the CCP and maintaining pH values close to 11.0.

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