

Conductive Cement Pastes with Carbon Fibers as Anodes in the Electrochemical Chloride Extraction

M. J. Pellegrini Cervantes¹, C.P. Barrios Durstewitz^{1,*}, R. E. Núñez Jaquez¹, F. Almeraya Calderón², M. Rodríguez Rodríguez¹, J.H. Castorena Gonzalez¹, E. Garcés-Velázquez³, E.E. Maldonado-Bandala³, D. Nieves-Mendoza³, J.P. García-Contreras⁴

¹Universidad Autónoma de Sinaloa Facultad de Ingeniería Mochis, Fuente de Poseidón y Prol. Ángel Flores S/N, Los Mochis, Sinaloa, México.

²Universidad Autónoma de Nuevo León. FIME - Centro de Innovación e Investigación en Ingeniería Aeronáutica. Av. Universidad s/n. Ciudad Universitaria. San Nicolás de los Garza, N.L., México.

³Universidad Veracruzana, Facultad de Ingeniería Civil-Xalapa, Circuito Gonzalo Aguirre Beltrán s/n, Zona Universitaria 91000, Xalapa, Veracruz, México.

⁴Facultad de Ingeniería, Universidad Autónoma de San Luis Potosí (UASLP)), E. D. C. Vázquez.

*E-mail: durstewitz@uas.edu.mx

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The use of cement-based multifunctional materials as anodes in the protection against corrosion and in the repair of reinforced concrete structures are actually of great interest among scientists and engineers due to the benefits that present the methods of nondestructive rehabilitation. By nature, cement based materials have acceptable mechanical properties, however their electrical properties are deficient; the addition of conductive carbon materials such as graphite powder, coke powder or carbon fibers makes them multifunctional materials of suitable mechanical and electrical properties. This paper presents the study of the performance of a conductive cement paste (CCP) with the addition of crushed coke and carbon fiber (CF) as anode in the electrochemical chloride extraction in contaminated concrete with 2.31% chloride according to the weight of cement, studying the PCC as an alternative use of multifunctional materials in electrochemical techniques. A comparative is made in the performance of 3 anodes: stainless steel mesh, CCP without addition of carbon fiber and CCP with addition of 0.90% of CF in volume fraction, with the use of an alkaline electrolyte of lithium borate and current density of 4.0 A/m² on the steel surface. In addition, it was monitored subsequent corrosion potentials to Electrochemical Chloride Extraction (ECE) and pH variation in electrolyte and concrete mass. The anode of CCP with addition of CF presented chloride contents of 0.22% after 21 days of ECE, with free extractions of chlorides with up to 90.4% CCP with CF, while the technique with stainless steel mesh presented a 77.6%. The results provide an important advance in the improvement of the performance of anodes of multifunctional materials in electrochemical techniques used in rehabilitation of reinforced concrete structures contaminated with chlorides.

Keywords: cement conductive paste, carbon fiber, crushed coke, corrosion potential, electrochemical techniques.

1. INTRODUCTION

Natural protection against corrosion of reinforcing steel in concrete is usually lost due to the arrival of chlorides to the reinforcement [1]. The consequence is a process of active corrosion that leads to reduce the service life of reinforced concrete structures. Conventional methods to repair the concrete affected by these aggressive agents aim to remove all the contaminated concrete, to clean the reinforcement and apply a new layer of concrete or mortar free of the contaminants, procedures that generate pollution by noise and waste. In recent decades it has been developed and implemented a number of electrochemical techniques with features of non-destructive character, among them stands out the ECE, which consists of applying a direct current with current density less than 4A/m^2 between the reinforcing steel that acts as a cathode and an external electrode which serves as the anode, usually the anode is a steel mesh or activated titanium immersed in alkaline solution. The ECE normally requires several weeks of application [2].

Moreover, cement based materials are poor conductors of electricity. The increased performance in their electrical properties is achieved by additions of conductive carbonaceous materials such as graphite powder or crushed coke [3]. Furthermore, Carbon fibers are electrically conductive and are also effective as additions in the cement matrix to achieve a material with better electrical conductivity characteristics. Electrically conductive particles, such as graphite powder, are less effective due to its low ratio aspect. However, the particles tend to be much cheaper than fibers and low cost is important for the viability of concrete technology. The combination of a material with structural characteristics and a material with conductive characteristics, results in what is known as a multifunctional material. Some authors have made research concerning conductive cement based materials with applications as: electrochemical extraction, cathodic protection, percolation threshold determination, electrical contact, sensors and corrosion, among others [6-17].

The idea of a layer of conductive cement based material as electrode in electrochemical techniques to mitigate or prevent corrosion in concrete structures is not new, in the United States in the early seventies Stratfull used a conductive layer asphalt-base elaborated, concrete and crushed coke as anode in a system of cathode protection by impressed current and settled on a bridge [18]. Moreover, Perez et al. used a layer of conductive cement based material added with graphite powder as an auxiliary electrode in the electrochemical chloride extraction demonstrating that the use of this material, presenting similar efficiencies to an auxiliary electrode mesh Ti-RuO_2 is feasible [6].

The present paper aims to demonstrate the feasibility of using a layer of CCP with addition of crushed coke and carbon fiber as an auxiliary electrode in the chloride electrochemical extraction in contaminated concrete referring to metal electrode on concrete surface.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Reinforced concrete specimens

The reinforced concrete test specimens were 7.0 cm in diameter and 14.0 cm high cylindrical with 3/8" reinforced steel rod embedded 10.0 cm in the specimen center, the curing was of 28 days at a 100% relative humidity and a temperature of $25\text{ }^\circ\text{C}$. To prepare the mixture, 2.6% NaCl was previously

dissolved regarding the cement weight in distilled water, the design was by method of absolute volumes of the Portland Cement Association (PCA) for a design strength of 280 kg/cm², maximum aggregate size of 1/2" silica sand with fineness modulus of 3.0 and slump of 75-100 mm, proportions of the concrete are shown in *Table 1*.

Table 1. Dosage 1.00 m³ of concrete contaminated with NaCl

Component	Quantity (kg)
Distilled water	228.00
Silica sand	655.55
Gravel TMA ½"	957.60
Compoused Portland Cement 30R tipo	456.00
Sodium chloride	11.80

A CCP layer of 1.0±0.1 cm thick was applied on the curved surface of the specimen with two ¼" graphite rods embedded as main anodes in opposite ends of the tube without CCP in the lower place or top. A hardening period of 24 hours was maintained for the CCP before curing, which was carried out in distilled water for 7 days at 100% relative humidity and at 25 °C temperature.

2.1.2. Conductive cement pastes

2 Types of mixtures for the CCP were prepared, the first with crushed coke and no CF and a second with crushed coke together with CF of 10 µm diameter, the weight ratios relative to Portland Cement 30R type I of 0.50 distilled water, 0.15 micro silica and 1.00 crushed coke. In the meantime, the volumetric ratio respect to the total volume of the mixture of 0.9% CF and 0.15% antifoam. Furthermore, according to method BET using 5.0 degree Nitrogen, the density specified of crushed coke is 1.85 and for CF is of 1.76, while its surface area is 2.29 and 0.227 m²/gr, respectively.

2.2. Methods

2.2.1. Electrochemical chloride extraction

2.2.1.1. Anodes

The anodes used were: Stainless steel mesh, CCP without CF and CCP with CF, all considered inert anodes.

2.2.1.2. Electrolyte

The function of alkaline electrolytes is to minimize the acidification and the evolution of chlorine gas in inert anodes [19]. The electrolyte used a borate alkaline solution of 0.2 M Lithium, prepared with distilled water, 14.4 g. of LiOH and 12 g. of H₃BO₃ per liter of solution, as recommended by NACE SP0107-2007. These solutions are convenient where there is the possibility of alkali-silica reactions in the concrete. After placement of the electrolyte lithium borate, the specimens were kept immersed for 24 hours before the application of ECE.

2.2.1.3. Current Density applied and treatment duration.

The accumulated charge for a minimum treatment of charge density per unit area of steel is 600 to 1500 A.h/m², according to NACE SP0107-2007. ECE was applied for 21.0 days with a cumulated charge superior to 1500 A.h/m² and current density of 4.0 A/m² in steel surface, upper limit of the recommendations of NACE SP0107-2007. Application periods were of 8.0 and 21.5 days as shown in Table 2.

Table 2. Application period of ECE

Specimen	Anode	Volumetric Fraction of CF in CCP	Application days	Cumulated charge calculated (A-h/m ²)
Reference	-	-	0.0	0.0
Mesh-8	Stainless steel mesh	-	8.0	768.0
Mesh-21		-	21.5	2064.0
CCP-8	CCP	0.0	8.0	768.0
CCP-21			21.5	2064.0
CCP/FC-8		0.9	8.0	768.0
CCP/FC-21			21.5	2064.0

2.2.1.4. Arrangement for the technique application.

For measuring and adjusting the current during application of ECE, the current was applied by a variable direct current source, prior connection of specimens in parallel circuits in groups of 3 with fixed resistance of 1.0 Ω and 1.0 kΩ rheostat per circuit, as figure 1.

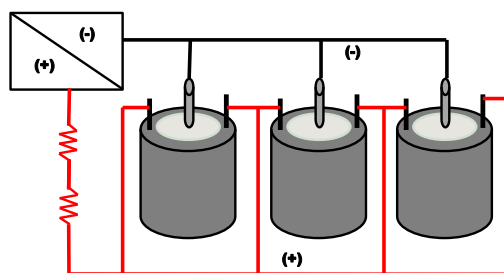


Figure 1. Circuit used in parallel in ECE arrangement

Individual test arrangements for ECE with metal mesh, CCP with or without CF were installed under the same conditions, unlike the connection of the anodes because they are of different nature, as shown in Figure 2.

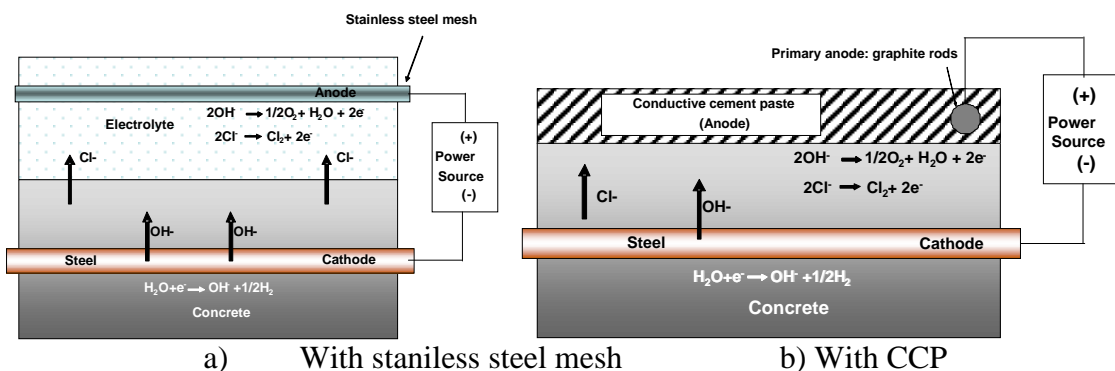


Figure 1 EEC Experimental arrangement

2.2.2. Free chlorides percentage

NACE SP0107-2007 recommendations indicate, as acceptable limit values, 0.40% for the percentage of free chlorides with respect to the weight of the cement at one diameter distance of the steel surface. The content of free chlorides was performed by chemical titration according to ASTM D1411-99 [20]. 30 g samples were taken with drill and 1/4 "drill bit, to 1.0 and 2.0 cm. from the reinforcement surface for the case of the concrete and in the center of the layer thickness for the case of CCP at 0.0, 8.0 and 21.0 days of application of ECE, as Figure 3.

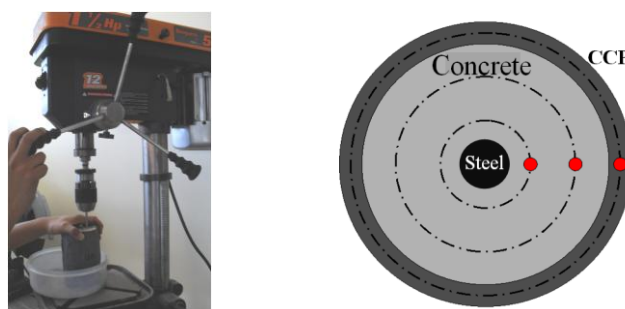


Figure 2. Mechanical extraction of powdered sample of concrete and CCP.

2.2.3. pH of electrolyte and concrete.

Electrolyte and concrete pH was determined weekly with digital pH meter. It was performed in the concrete at 1.0 cm of the reinforcement at 21 days of ECE, it was obtained 1g. of sample powder, it was dissolved in 25 ml. of distilled water and stirred for 40 min. Filtering further the solution prior to take reading.

2.2.4. Corrosion potential

Subsequent to ECE, the test specimens remained immersed in distilled water in the process of depolarization for 30 days. Its corrosion potential (E_{corr}) was monitored with respect to the standard calomel electrode (SCE) to constant potential for 7 days, as recommended by ASTM C-876-91 [21].

3. RESULTS AND DISCUSSION

The direction of diffusion of chloride to the surface of the reinforcing steel is reversed to the concrete surface by applying negative charge on the reinforcing steel. In investigations concerning ECE were applied accumulated charges of 1114, 1200, 5400 and 3720 A.h/m² with chloride extraction of around 50% [6, 22-24]. Using CCP for 7 days of the application of the ECE with accumulated charge of 768.1 A.h/m² respect to the reinforcement surface, the percentages of chloride extraction at 1.0 cm of the reinforcement decreased 1.9% for CCP and 54.6% with CCP/CF, with percentage of chlorides in the CCP of 61.4% respect to CCP/CF. While at 2.0 cm from the reinforcement the decreases were 1.1 and 23.0%, with increases in the CCP/CF of up to 1.3% as shown in Figure 4. This is attributed to the uniform conductivity in the anode mass which is achieved with to the addition of Carbon fiber.

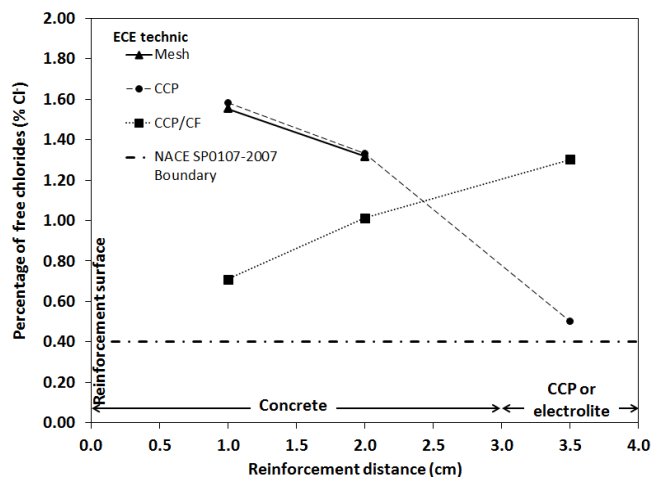


Figure 3. Free chlorides profile after 7 days of ECE.

The percentages of chloride extraction at 1.0 cm of the reinforcement decreased 8.6% for CCP and 57.1% with CCP/CF at 21 days of EEC with cumulative charge of 2057.0 A.h/m², with percentage of chlorides in the CCP of 29.0% respect to CCP/CF. In the meantime at 2.0 cm of the reinforcement the decreases were 4.2 and 31.2%, with increases in the CCP/CF of up to 2.29% as shown in Figure 5. The chloride percentage for the CCP/CF anode was 0.22% to 1 cm. of the reinforcement at 21 days of application of the ECE technique, less than the recommended limit in NACE SP0107-2007 [25] of 0.40%. The best performance of the CCP when having a carbon fiber volumetric fraction of 0.009, is attributed to its ability to maintain higher pH than techniques using only CCP or stainless steel mesh. Furthermore, by providing the CF greater contact between the carbonaceous material of the cement matrix, the contact area is greater between electrolyte and anode, thereby favoring decreasing acidification of lithium borate and evenly distributing the charge density on the concrete surface, allowing an homogeneous EEC in the concrete mass.

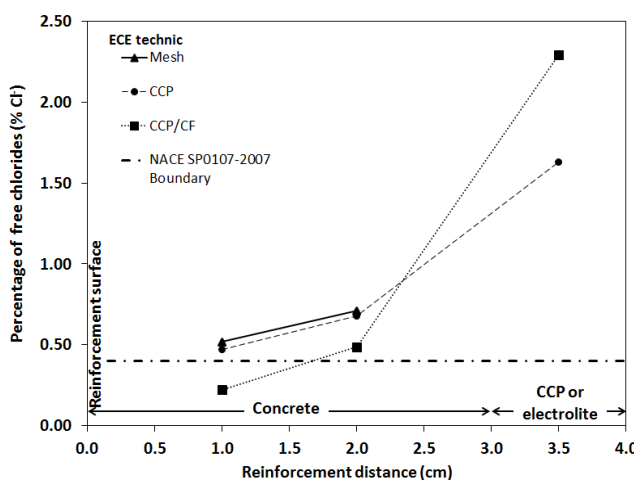


Figure 4. Free chlorides profile after 21 days of ECE.

The electrolyte pH at the beginning of the application of the EEC was 14.0, in the development of EEC acidification of the solution showed, the largest decreases were when using steel mesh as anode with decreased pH to 29.7%, ECE decreased to 21.8% and CCP without CF decreased to 29%, as shown in Figure 6. The application of ECE presented the formation of oxygen gas and water molecules preceded by the presence of OH⁻ ions in the anode, according to the mechanism $2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$ where OH⁻ ions become in oxygen and water molecules. Moreover, it follows that chlorine gas evolution does not occur when pH remains above 7.0 in the electrolyte.

The success of the Lithium Borate buffer solution used as electrolyte is in function on its ability to maintain Ph stable with possible decreases. As shown in Figure 6, the general tendency of pH in the electrolyte is to decrease because it is a buffer solution. Adding CF to the CCP increases the surface area of the carbonaceous material, as well as the adhesion properties in the cement matrix of CCP in addition to achieving a more effective distribution of the charge, which increases the performance of the ECE. The acid medium generated in the electrolyte, for the case of CCP without CF, caused

deterioration of the cement matrix with graphite powder release. As for CCP/CF, degradation was at very low levels with minimal release of carbonaceous material. This is attributed to improved performance in the distribution of charge density, coupled with the increased adhesion generated within the cement matrix and the grains of carbonaceous material provided by the CF. On the other hand, regarding the pH of the concrete at 1.0 cm. of the reinforcing steel for 21 days ECE, remained without significant variation in the order of 12.0 for all anodes studied, suggesting a passive state of reinforcing steel.

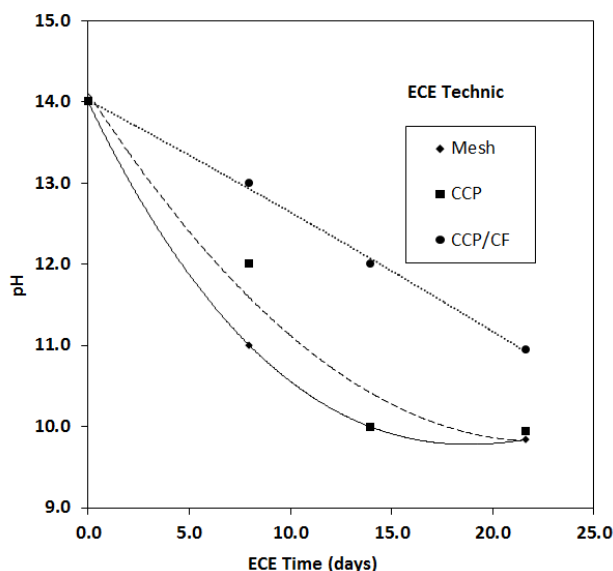


Figure 5. pH vs. time of lithium borate anolyte during the electrochemical treatment.

Following 28 days of EEC, the E_{corr} of the test specimens with metal mesh anodes, CCP without CF and CCP/CF, decreased to values -1112, -1137 and -1134 mV, respectively. These values increased in the process of depolarization to stabilize at an average time of 21 days.

The E_{corr} is a criterion for determining the state of corrosion of reinforcing steel according to ASTM C-876-91 [21]. Figure 7 shows the E_{corr} values obtained after depolarization, the reference test specimen is in an area of 90% probability of showing an active corrosion process, while the test specimens with metal mesh anodes and CCP without the addition of CF in an uncertain area. CCP/CF test specimens were in an area of 10%. E_{corr} in all test specimen was above reference, the CCP and CCP/CF test specimens showed higher values than the rest. This is attributed to higher performance developed by cementitious pastes CCP and CCP/CF to induce the migration of chlorides to the concrete surface or well to distant areas of the surface of steel reinforcement.

Another criterion for determining the state of corrosion of reinforcing steel is the current density I_{corr} with reference to the limits recommended in the corrosion Manual, Corrosion Evaluation and Diagnosis of The Reinforced Concrete Structure (CDRCS). Figure 8 shows I_{corr} values obtained after depolarization, all test specimens are in a very high corrosion area with lower corrosion in CCP/CF and greater in the reference test specimen.

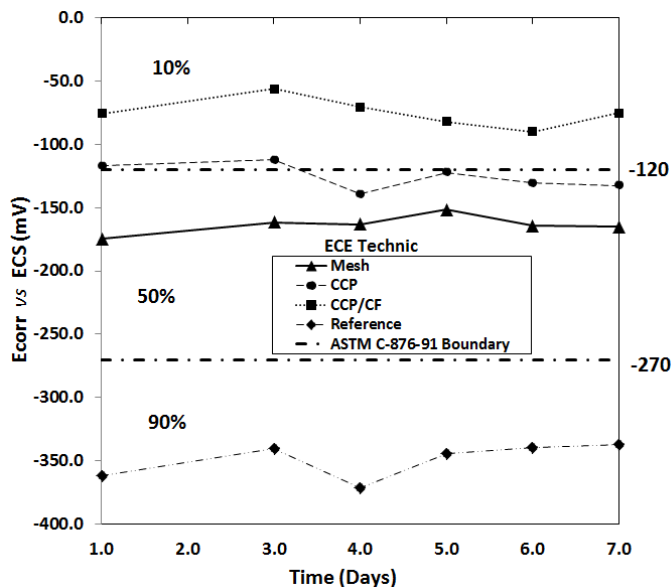


Figure 6. Ecorr depolarized specimens with 21 days of ECE.

Corrosion levels were not brought down, however the use of CCP contributed to obtain lower Icorr values. ECE technique is not corrosion eliminating but a technique to prevent it by the extraction of chlorides. Corrosion processes already active do not decrease its propagation by the application of the ECE, but it is possible to prevent the generation of new pits in the surface of the reinforcing steel.

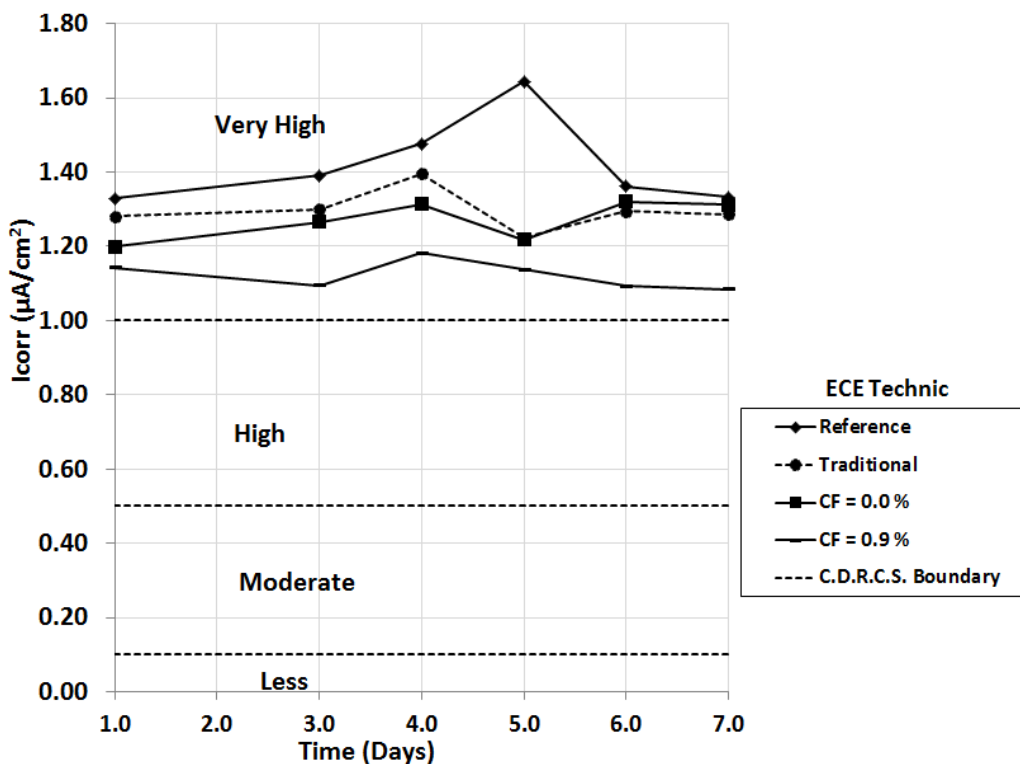


Figure 7. Icorr of depolarized test specimens with 21 days of ECE.

Perez et al, with the use of a conductive paste of cement with a proportion in weight of cement: graphite: water of 1.0: 1.0: 1.0 as counter-electrode and titanium mesh as anode in the ECE, show chloride extractions of 65 and 41% of its initial content with streams of 5.0 and 1.0 A/m² with respect to the surface of the steel, respectively [6]. Furthermore, A. Cannon et al, with the use of cement paste: overspray graphite powder and titanium mesh, achieved efficiencies of 79% in both cases [7]. Adding carbon fiber to the cement achieves conductive paste decreases in chloride content of up to 90.4% of free chlorides extracted for a volumetric fraction of the carbon fiber addition of 0.9, compared to 77.6% of the traditional technique, which uses a stainless steel mesh as counter-electrode.

4. CONCLUSIONS

- A CCP with or without added CF used as an anode in the ECE has adequate performance in the rehabilitation of reinforced concrete contaminated with chlorides.
- A CCP with addition of CF in 0.009 volumetric fraction used as anode in the ECE presents efficiency in chlorides extraction superior to a stainless steel mesh anode. It also decreases the possibility of new pits on the steel surface and achieves corrosion potentials corresponding to areas of 10% chance of active corrosion processes according to ASTM C-876-91, while an anode of stainless steel mesh remains in uncertain area.
- The use of CF in a CCP anode used in ECE favors pH conservation and prevents the release of the carbonaceous material in the interface anode-electrolyte.

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