

# **ENHANCEMENT OF ELECTROCHEMICAL CHLORIDE REMOVAL USING CORROSION INHIBITORS**

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## **Abstract**

Corrosion inhibitors can be introduced through concrete pores under the action of an electrical field. In this work, migration of corrosion inhibitors from the surface of the concrete, simultaneously to Electrochemical Chloride Removal (ECR), is considered. Two methods are proposed: 1) Connection of rebar as cathode for application of cationic inhibitors, and 2) Connection of rebar to an external cathode for application of anionic inhibitors. Results show that the migration of inhibitors, simultaneously to ECR improves the efficiency of the treatment by removing more chlorides and enhancing the passivation process of the reinforcement after the treatment.

## **1. INTRODUCTION**

The rehabilitation of structures due to the presence of important areas damaged by the corrosion of the rebars is frequently needed. The most traditional technique of rehabilitation is based on removing the contaminated concrete around the damaged area. In recent years, advanced techniques based on the electrochemical removal of the aggressive have shown to be very promising: Electrochemical ReAlkalisiation (ERA) and Electrochemical Chloride Removal (ECR). Nowadays, experience exists with these methods, both in laboratory and on-site [1-5].

ECR is a non-conventional repair technique which considers a temporal connection of a direct current between an external anode placed on the surface of the concrete and the rebar connected as cathode. In this way, chlorides are expected to migrate from the reinforcement to the external anode. A simultaneous increase of the alkalinity in the area around the rebar takes place because of the very cathodic potentials reached by the reinforcement connected as cathode [2]. Furthermore, the application of ECR as repair method requires to assure the passivation of the reinforcement after the treatment.

One of the main limitations of these techniques is to guarantee that concentration of chlorides remaining near the surface of the rebar is not sufficient to reactivate the corrosion of the reinforcements after the treatment. Besides, secondary effects as consequence of the

electrochemical reactions occurring at the rebar level can not be neglected, as for instance: the risk of hydrogen embrittlement of the rebar due to the very negative polarisation potentials reached during the treatment, higher when the treatment is applied to prestressed structures [6] and the high increase of pH and alkalis in pore water of the concrete near the reinforcement that can induce alkali-silica reaction in sensitive aggregates [7]. Other uncertainties still remain once the treatment is finished related to the electrochemical response of the system. The high voltage applied during the treatment polarizes strongly the rebar to very cathodic potentials, far from the equilibrium, and then the passivation of the reinforcement has to be reached when the electric field ceases. However, passivation of the rebar is only achieved some days after the treatment is finished [8,9]. High values of corrosion current densities are measured during these days and cathodic corrosion potentials are maintained during some months after the treatment. Furthermore, recent studies have demonstrated that this type of treatments has temporal efficiency and the new passive state reached after the treatment is lost with time [10].

Surface corrosion inhibitors are also considered as novel repair technique of existing structures, but several limitations make unpractical the method: the penetration of most of the active inhibitor consumes long time when it has to penetrate dissolved in the water inside the pores of the concrete, besides some inhibitors react with the concrete avoiding the penetration [11,12]. Although recently vapor-phase inhibitors are employed to allow faster penetration [13], the efficiency of the method is not sufficiently demonstrated yet.

The application of corrosion inhibitors on the concrete surface can be also considered as complement of ECR. The migration of an inhibitor applied on the surface of the concrete by the connection to an electric field, forcing the movement of the constitutive ions of the inhibitor directly to the rebar, has been already reported elsewhere [8,14,15]. The connection of the rebar to the negative pole of the power supplier, as in the electrochemical repair methods, allows accelerating the penetration of cationic inhibitors from the anode side located on the surface of the concrete towards the rebar connected as cathode. However most of the previous studies either did not obtain any conclusion about the rebar corrosion [16] or were focused in evaluating the transport of the inhibitor under the electric field but did not investigate the corrosion resistance of the rebar as consequence of the treatment [17,18].

The present work has been focused on evaluating the synergic effects associated with the simultaneous application of an electrochemical chloride extraction treatment and penetration of corrosion inhibitors by migration through the concrete pores. The recovering of the passive state after the treatment was considered.

## **2. EXPERIMENTAL METHODOLOGY**

Standard mortar samples of 2x5.5x8 cm were fabricated using CEM I and deionised water containing 1% NaCl dissolved, in order to guarantee propagation of corrosion from the beginning of the tests. The mortar specimens were cured in a thermostatic chamber ( $21\pm 2^\circ\text{C}$ ) and at  $98\pm 2\%$  of Relative Humidity (RH), for nearly three months before the treatment and also after the ECR treatments had finished. The mortar samples have embedded two reinforcements of 6 mm in diameter, showing an exposed surface of  $5.6\text{ cm}^2$  each rebar.

The corrosion state at the level of the reinforcements was periodically monitored employing two electrochemical measurements: 1) Corrosion potential ( $E_{\text{corr}}$ ) using a silver/silver chloride electrode (the values in present document are expressed vs. Standard

Calomel Electrode, (SCE), and 2) Polarisation Resistance,  $R_p$ , and further estimation of the corrosion current density ( $i_{corr}$ ).

The chloride extraction treatment was carried out using a conventional procedure for electrochemical repair treatments: connecting the rebars to the cathode of an electrical supplier and an external mesh of titanium oxide to the anode. The anode is immersed in water in order to guarantee electrical connection through the mortar surface. An electric field of 12 V was connected between the anode and the cathode. The connection is maintained for 5 days. The arrangement employed is shown in figure 1-left, where the transport of anions to the anode and the transport of cations to the rebar connected as cathode are indicated. Also the electrochemical reactions taking place on each electrode as consequence of the connection of the electric field have been resumed.

The application of inhibitors during the repair treatments was investigated by locating a solution containing the inhibitors on the surface of the mortar samples. Depending on the nature of the inhibitor the arrangement employed was different.

- 1) For migration of cationic inhibitors: The arrangement was the same to that used for conventional ECR, but using a solution with the cationic inhibitor instead of using water in the ponding in contact with the anode. Two different organic-based inhibitors were considered: 0.2M solution of ethanolamine and 9% vol. solution of a commercial mixed inhibitor based on amino-alcohol. The transport of the cationic active group of the inhibitor (group amine,  $NH_2^+$ ) through the mortar cover to the rebar was favored by the electrical field, simultaneously to  $Cl^-$  extraction. This arrangement has been schematized in figure 1-left.
- 2) For migration of anionic inhibitors: the methodology was modified. The electric field was connected between two external electrodes consisting of titanium oxide mesh acting as cathode and anode, respectively. Simultaneously, the rebars were connected to the external cathode. The external cathode was immersed in a solution containing  $Ca(NO_2)_2$  0.5M while the anode was located at the opposite surface of the mortar sample and located in a ponding filled with water. In figure 1-right has also been included the scheme of this arrangement. The arrangement allowed fulfilling the objective of electrochemical chloride removal with simultaneous penetration of nitrites, but maintaining the rebar at potentials of immunity against corrosion. With this arrangement the extraction of chlorides takes place in the same direction that in a conventional ECR treatment, from the mortar bulk to the external anode, while the migration of nitrites from the cathode to the anode was promoted.

The polarization potentials of the rebars were measured during the treatments. The samples were maintained in a chamber at  $(21\pm 2^\circ C)$  and at  $98\pm 2\% RH$  after the treatments, during at least three months in order to follow the passivation process of the reinforcement, by periodic measurements of  $E_{corr}$  and  $I_{corr}$ . At the end of the tests, the samples were broken and the visual observation of the rebars was made to confirm the superficial state. The content of chlorides at the rebar level was also determined.

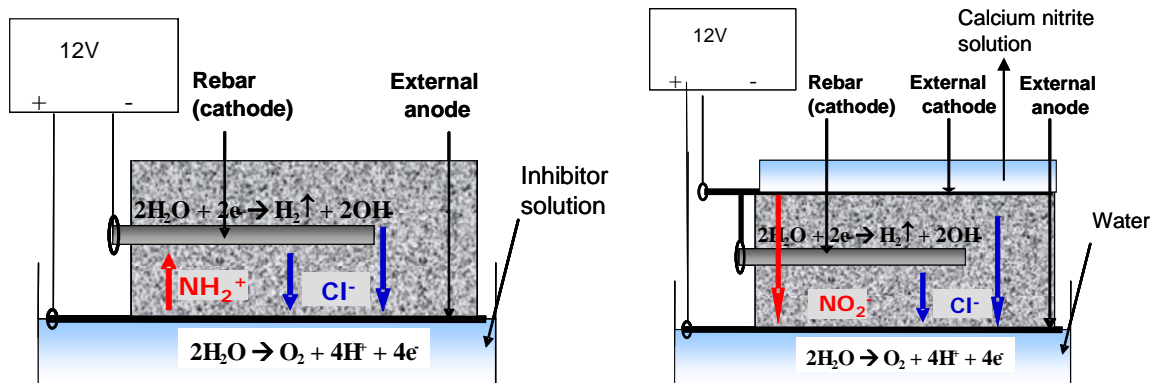


Figure 1: Schemes of the arrangements employed for the samples treatment. Left, for ECR with simultaneous introduction of cationic inhibitors. Right, for ECR with simultaneous penetration of anionic inhibitors.

### 3. RESULTS AND DISCUSSION

#### 3.1 ECR with simultaneous migration of cationic inhibitors.

The application of two organic-based inhibitors containing amine ions as active group has been studied. The migration of this cationic group towards the rebar simultaneously to the ECR from the bulk of the concrete is expected to take place during the treatment. Following this procedure two positive actions were promoted: 1) decrease of the chloride content in the mortar samples and 2) the penetration of the corrosion inhibitor up to the level of the rebar for improving the generation of the passive film after the treatment.

The high cathodic polarization registered during the connection of the rebars as cathode is given in figure 2. The values are similar for the treatments with the inhibitors, independently of their composition. The potential values recorded were  $-9\text{ V, SCE}$  which has to be associated with an intensive generation of  $\text{OH}^-$  around the rebar. However lower values than  $-10\text{ V, SCE}$  were measured without penetration of the inhibitor. Besides, these low potential values can favor the reduction of the corrosion oxides previously formed during active corrosion process.

After disconnection of the electric field the ability of the system to recover the passivation state was followed. In figure 3 has been included the evolution of  $E_{\text{corr}}$  (left) and  $i_{\text{corr}}$  (right).

The connection of the rebar as cathode to make a chloride extraction simultaneously with the inhibitor migration also promotes significant cathodic polarizations of the rebars that were maintained some days even after switch-off the electrical field. High corrosion rates,  $i_{\text{corr}}$  after the finalization of the treatment were registered in similar order than those observed in the case of chloride removal without simultaneous introduction of inhibitors. This response of  $i_{\text{corr}}$  is in agreement with the evolution of  $E_{\text{corr}}$ . At least 15 days after finalization of the electrochemical treatments were needed to recover anodic values of  $E_{\text{corr}}$  typical of negligible corrosion. Similarly the  $i_{\text{corr}}$  decreases to values below  $0.2\ \mu\text{A}/\text{cm}^2$ . The effect of the inhibitor can be observed mainly during the first days after the disconnection of the treatment, by an enhancement in the rate of passivation recovering of the rebars. The improvement on the efficiency of the treatment with the migration of cationic inhibitors is also detected in the amount of chlorides removed from the rebar level respect to the content before the treatment:

Percentages of 54% Cl<sup>-</sup> removed without penetration of inhibitor and while 67% and 64% Cl<sup>-</sup> with the simultaneous introduction of the ethanolamine and the commercial inhibitor, respectively.

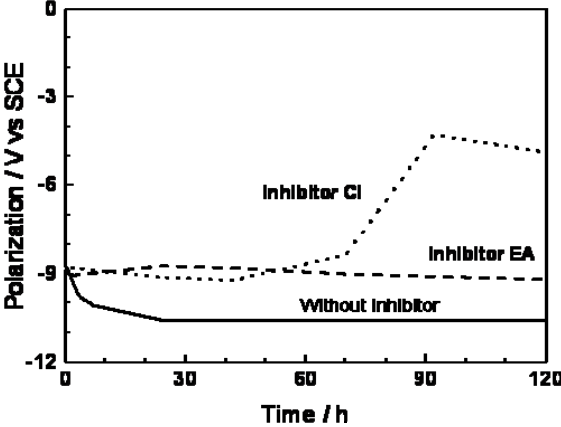


Figure 2: Cathodic polarization of rebars during the connection of the electric field for the chloride extraction treatment with simultaneous migration of Ethanol Amine (EA) or Commercial Inhibitor (CI).

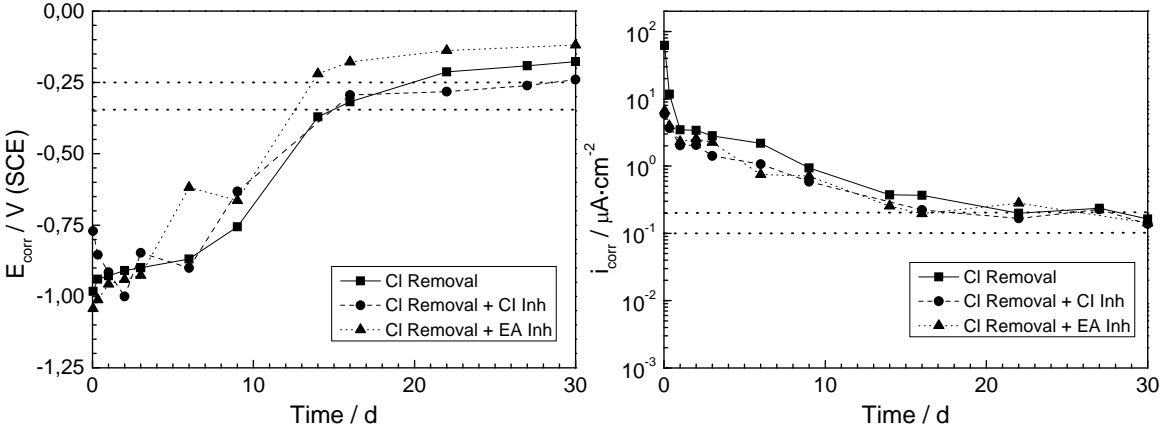


Figure 3. Evolution of E<sub>corr</sub> (left) and i<sub>corr</sub> (right) after the application of the electric field for the chloride extraction treatment with simultaneous migration of Ethanol Amine (EA) or Commercial Inhibitor (CI).

**3.2 ECR with simultaneous migration of anionic inhibitors.**

The connection of the rebar to the cathode has been considered in this case. The arrangement for introduction of nitrites from the cathodic compartment containing the external cathode to the anodic compartment containing the external anode is considered. Cathodic polarization potentials between -1 to -2V (SCE) were measured on the rebars during the treatment, as observed in figure 4. These potentials are considerably less cathodic than the

polarization potentials registered with the treatment without migration of nitrites (the potentials were below -10V(SCE)).

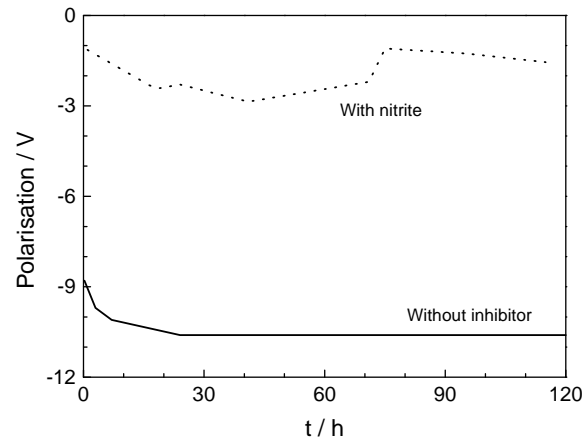


Figure 4: Polarisation of rebars during treatments of chloride removal without and with introduction of nitrites.

After the ECR with connection of the rebars to the external cathode the evolution of the electrochemical response of the rebars was monitored. In figure 5 the evolution of  $E_{corr}$  and  $i_{corr}$  values recorded are represented. In these figures, the response of the rebar after a conventional treatment for chloride extraction with the rebar acting as cathode and without introduction of nitrite has been included as reference case. The evolution to passivity of the rebars has taken place faster when the introduction of nitrite is considered simultaneously to the ECR. In addition to this, the anodic inhibition action of nitrite is observed reaching more anodic  $E_{corr}$  values once passivation has been reached. The passive state is maintained for at least 30 days.

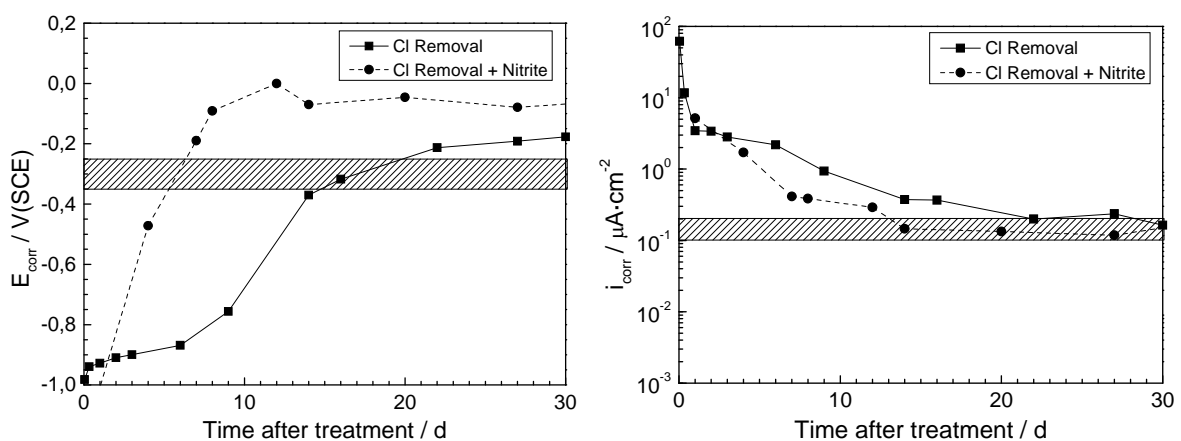


Figure 5: Evolution of  $E_{corr}$  (Left) and  $i_{corr}$  (Right) after the disconnection of the electrochemical treatment of chloride removal with and without simultaneous introduction of nitrite as corrosion inhibitor.

The positive effect of the nitrite on the repassivation of the rebars is also confirmed with corrosion current density measurements as shown in figure 5-right. The anodic character of nitrites enhances the formation of protective oxides on the rebar that promotes the protection of the reinforcements only 10 days after finishing the electrochemical treatment, values of  $i_{\text{corr}} < 0.15 \mu\text{A}/\text{cm}^2$  indicating that the passive state had been reached, while this did not happen before 20 days without inhibitor migration. The efficiency of the ECR treatment is reflected in 75% total chloride removed from the mortar at the rebar level when introducing the nitrite, respect to 54% without introducing the inhibitor.

The advantage of ECR with simultaneous introduction of inhibitors in comparison with conventional ECR is going to be associated with the improvement of the efficiency of the treatment during the regeneration of the passive film enhancing the protection of the rebar, and higher efficiency in the amount of chloride removed.

The mortar samples were broken after 3 months of disconnection the electrical field, to confirm the superficial state of the rebar and to evaluate the efficiency of the treatment. The visual inspection of the rebar shows a free-oxides surface, without any sign of corrosion, confirming the efficiency of the treatment.

#### 4. CONCLUSIONS.

- It is possible to accelerate the transport of corrosion inhibitors by migration under the presence of an electric field.
- The connection of the rebar as cathode promotes high values of corrosion current density after the electric field applied is disconnected. However, the regeneration of the passivity takes place in shorter time when inhibitors are penetrated simultaneously.
- The transport by migration of inhibitors enhances the efficiency in extraction of chloride and further repassivation of the rebar.
- A mixed arrangement considering both the connection of two external electrodes and the rebar as connected to the cathode is needed for simultaneous migration of anodic inhibitors and chloride removal.

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