Electrochemical chloride removal in reinforced concrete structures: Improvement of effectiveness by simultaneous migration of calcium nitrite

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A B S T R A C T

Electrochemical Chloride Extraction (ECE) is becoming a common methodology for repairing reinforced structures. Also the application of corrosion inhibitors on the concrete surface for its penetration its getting more and more interesting as protective method against corrosion of reinforcements. In this sense, the migration of corrosion inhibitors can be promoted by the application of an electric field, enhancing in this way the transport of the inhibitor. In present work, the simultaneous application of both technologies is proposed. The migration of nitrite to the rebar is promoted during the application of an ECE treatment by modifying the classical configuration through the connection of an external cathode to the rebar. The electrochemical response of the rebar after the treatment has been evaluated by corrosion potential and polarization resistance measurements. The efficiency of the treatment was confirmed by the visual inspection of the rebar and the analysis of chloride and nitrite at the level of the rebar.

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1. Introduction

Nowadays an important investment in repairing and retrofitting reinforced concrete structures is being carried out due to the aggressiveness of the environment and the ageing of the concrete. In this sense, several techniques to repair and rehabilitate reinforced concrete structures have been developed to optimize both the cost and the efficiency of repair projects [1,2]. The most conventional way to repair a reinforced concrete structure affected by corrosion is based on the removal of the concrete surrounding the rebar. Then, the oxides of the rebar are cleaned and a new layer of concrete or repair mortar is added.

The application of non-conventional repairing techniques is becoming more and more usual. The interest of these techniques, known as Electrochemical Maintenance Methods, lays mainly on the ability of removing the aggressive but maintaining the covering of concrete and allowing the passivation of the reinforcement [3–5]. Three main techniques are distinguished depending on the aggressiveness of the environment and on the type of structure: Cathodic Protection (CP) [6,7], Electrochemical Chloride Extraction (ECE) [8–11] and Electrochemical Realkalisation (ER) [12,13].

The Electrochemical Maintenance Methods (ECE and ER) are characterized by the application of a temporal cathodic current to the reinforcement connected as cathode by mean of an external anode located at the surface of the concrete [3–13]. The arrangement of these techniques enhances the formation of hydroxyl ions at the level of the rebar that support the alkalinity of the aqueous phase near the rebar area. In the case of carbonated concrete, the diffusion of OH^- through the pores promotes the realkalisation of the concrete. Furthermore, these procedures also promote the elimination of chlorides from the concrete.

Many uncertainties still remain concerning the performance of the system after the treatment is finished. The high voltages or currents applied during each treatment polarises strongly the rebar to very cathodic potentials, far from the equilibrium. Then the passivation of the reinforcement has to be recovered when the electric field ceases. Often the new passive state of the rebar is achieved some days after the treatment is finished [5] and high values of corrosion current densities are measured during these days. Recent studies [14] have also demonstrated that this type of treatments has a temporal efficiency since the new passive state reached after the treatment is lost with time, attributed to the diffusion of OH^- far from the rebar surface to the bulk of the concrete decreasing the pH at the rebar level and passivity is difficult to guarantee.

In a parallel way, the employment of additional protective methods has been considered to improve the service life of reinforced concrete structures to be exposed to hard aggressive environments. Among these methods, the corrosion inhibitors are the most versatile due to the possibility of application at any time

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along the service life of the structure. Corrosion inhibitors can be added to the fresh concrete, dissolved into the water used for mixing [15–17], or can be applied on the surface of the hardened concrete [16,18,19]. In later case, the solution containing the inhibitor has to penetrate through the pores of concrete towards the rebar. Different mechanisms of transport can be involved, as diffusion through the saturated pores, convection when the pores are not fully saturated (wetting/drying), and even, when an organic-based corrosion inhibitor is applied, the transport via the gaseous phase has been considered [20]. However, the transport of the inhibitor by these mechanisms generally is a slow process and the inhibitor takes long time to reach the rebar. Then, accelerated methods to promote the transport by migration of the ions of the inhibitor and to enhance the passivation process are being recently proposed [21–26].

The transport by migration of organic-based corrosion inhibitors has been proposed by applying a constant cathodic current density between the rebar connected as cathode and an external anode [21,24–28]. Furthermore, a procedure to introduce ionic or ionisable species, independently of the charge, in concrete structures has been proposed through the connection of two opposed external electrodes but with the rebar disconnected [22]. However, in presence of chlorides, the corrosion behaviour of the rebar can be affected by the effects of stray currents generated [29] and the connection of the rebar as cathode becomes necessary.

During ECE and ER treatments the rebar is connected as cathode. In this sense, the accelerated penetration of cationic inhibitors from the anode can be promoted [26]. However, the migration of anionic inhibitors (as nitrites) during an electrochemical repair treatment is also attractive. In fact, nitrites have shown the higher efficiency in corrosion inhibition [17] of steel rebars embedded in concrete.

In present work a modification of the ECE configuration is proposed to enhance the efficiency of the treatment by simultaneous application of an anionic inhibitor as calcium nitrite.

2. Experimental procedure

2.1. Materials

The study has been performed using on mortar samples fabricated with: OPC (marine and sulphate resistant, with low content aluminates and less than 0.4% of alkalis), standardise sand (from 0 to 4 mm size) and tap water. Water/cement ratio of 0.5 and sand/cement ratio of 3/1 have been employed. Sodium Chloride was added to the mixing water (1% Cl^- by mass of cement) to promote the corrosion onset from the beginning before applying the repair treatment.

Mortar samples of $20 \times 55 \times 80$ mm were fabricated with two rebars of 6 mm in nominal diameter embedded in each sample. The mortar specimens were cured for 3 months in a chamber at $98 \pm 2\%$ of humidity and 21 ± 2 °C. The corrosion state of the rebar was evaluated by electrochemical techniques before and after the electrochemical repair treatment had finished. Both the corrosion potential (E_{corr}) and

Polarization Resistance (R_P were periodically obtained. The R_P was measured by a linear scan sweep from -20 mV to $+20$ mV versus E_{corr} carried out at 10 mV/min. Applying the equation of Stern and Geary, the corrosion current density (i_{corr}) was deduced [30]. Mean values are given for each sample since two rebars were exposed to the treatment in each test.

The application of calcium nitrite was considered during the repair treatment by a ponding of 0.5 M $Ca(NO_2)_2$ solution on the mortar surface.

2.2. Experimental set-up

After a stable active corrosion was detected by the electrochemical measurements, the electrochemical treatment for chloride extraction with simultaneous introduction of calcium nitrite as corrosion inhibitor was applied to repair the corroding samples. A voltage of 12 V between an external anode and the rebar acting as cathode was applied during 5 days. The methodology applied considered also an external cathode short-circuited with the rebar and located on the concrete surface opposite to the anode [21]. After the treatment was finished, the electrochemical response of the rebars was periodically measured to evaluate the effectiveness of the treatment and the ability of repassivation of the rebars.

A ponding of 0.5 M $Ca(NO_2)_2$ was fixed on the surface of the concrete in contact with the external cathode during the treatment. A wetted sponge was continuously located on the surface of the sample in contact with the anode to assure the electrical conductivity through the pores. In this way, nitrites migrate through the concrete bulk from the cathode to the anode and the presence of the inhibitor at the level of the rebar after finishing the electrochemical treatment is expected.

Fig. 1 shows a scheme of the arrangement for the electrochemical treatment of chloride removal with simultaneous introduction of nitrite as corrosion inhibitor. During the connection of the electric field the current density passed through the rebar was monitored with a data-logger.

At the end of the tests, the samples were broken and the visual observation of the rebars was made to confirm the superficial state expected from the electrochemical measurements. Both Cl^- and NO_2^- content at the rebar level was determined.

3. Results

3.1. Electrochemical treatments of chloride removal and inhibitor penetration

The onset of corrosion of the rebar previously to the treatment was confirmed by E_{corr} and i_{corr} measurements in base to the criteria proposed in [31,32], $E_{corr} < -0.35$ V(SCE) and $i_{corr} > 0.2$ micro amperes per centimeter square ($\mu A/cm^2$). Then the ECE treatment with simultaneous introduction of nitrites was carried out by connecting the rebar as cathode and locating two external anodes at both sides of concrete (Fig. 1).

Cathodic polarization potentials between -1 and -2 V(SCE) were measured for the rebars during the treatment, assuring in this way the immunity of rebars against corrosion [33]. The introduction of nitrites from the cathodic compartment containing the external cathode to the anodic one containing the external anode is considered. In Fig. 2 the evolution of the current passed through the rebar during this treatment has been represented as function of the charge density passed during the experiment.
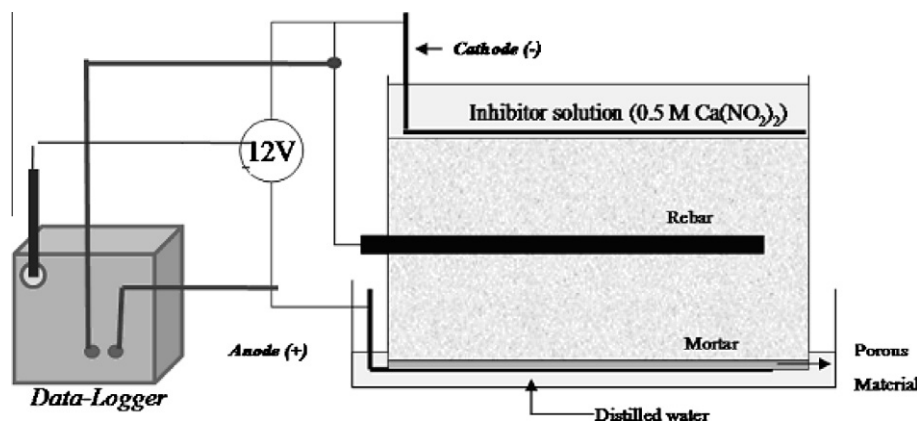

Fig. 1. Scheme of the arrangement for the treatment of electrochemical chloride removal with simultaneous penetration of nitrite.
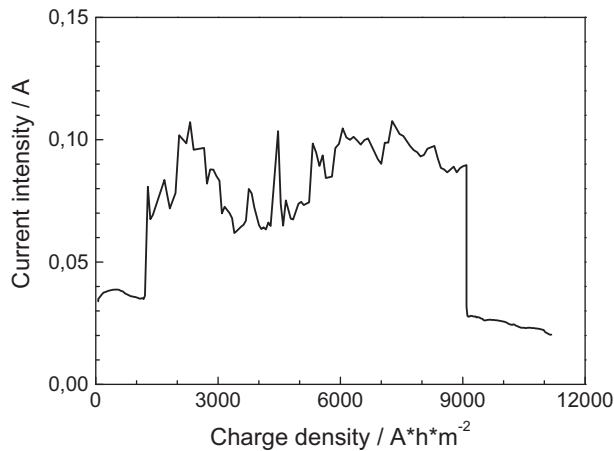
Fig. 2. Evolution of current in function of charge density passed during the treatment with rebar connected as cathode and simultaneous penetration of nitrite.

Fig. 4. Evolution of i_{corr} after the disconnection of the electrochemical treatment of chloride removal with and without simultaneous introduction of nitrite as corrosion inhibitor. Rebar connected to the cathode.

As can be observed from the figure, a sharp decay on current values is observed when a charge density near 9000 A h/cm^2 is reached. Similar behaviour has been published for electrochemical realkalisation treatments [5], associating this sharp drop of the current to an electro-osmotic flux through the concrete pores. Although in present case an electro-osmotic flux of nitrites between the external cathode and the rebar can not be ruled out, more experiments have to be done to confirm this hypothesis.

3.2. Effectiveness of treatment: electrochemical behaviour of rebars after treatments

The evolution of the electrochemical response of the rebars was monitored after the electrochemical treatment of chloride removal with connection of the rebar as cathode. In Figs. 3 and 4 the evolution of E_{corr} and i_{corr} values are plotted. In both figures, the response of the rebar after a conventional treatment for chloride extraction with the rebar acting as cathode without introduction of nitrite has been included as reference case.

The anodic effect of nitrite can be observed in Fig. 3, since the depolarization of E_{corr} to values indicating the passivity of the rebar takes place faster when the introduction of nitrite is considered simultaneously to the electrochemical treatment of chloride removal.
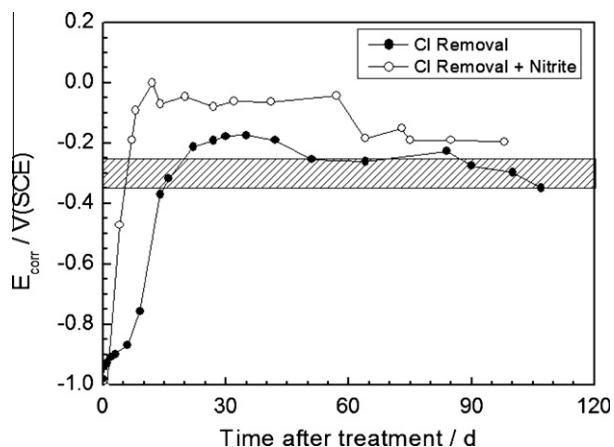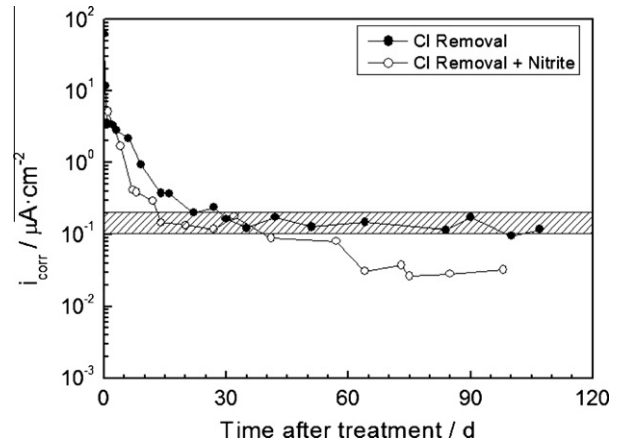
The positive effect of the nitrite on the passivation of rebars after the treatment is also confirmed with corrosion current density measurements, as can be deduced from Fig. 4. The anodic character of nitrites enhances the reaching of passive state on the rebar. After 10 days of finishing the treatment, values of $i_{corr} < 0.15$ micro amperes per centimeter square (μA/cm^2) indicating passivity has been reached. The i_{corr} values after the treatment with simultaneous penetration of nitrite more than 4 times smaller than in the case of the treatment without introduction of the inhibitor. Furthermore, this effect of nitrite on i_{corr} values is more remarked after 90 days of finished the treatment, indicating the improvement of the long-term efficiency of the treatment when a simultaneous penetration of nitrite is considered. In fact, lower i_{corr} values, indicating the passive state of the rebar, were maintained for more than 3 months confirming the formation of a new layer of iron protective oxides on the rebar surface and the efficiency of the treatment along the time. Then, the advantage of this method with simultaneous introduction of nitrite in comparison with the traditional method of electrochemical chloride removal should be associated with the improvement of the efficiency of the treatment during the regeneration of the passive film enhancing the protection of the rebar.

3.3. Visual inspection of rebars and analysis of chloride/nitrite content

After 3 months of disconnection of the electrochemical treatment the mortar sample was broken to confirm the superficial state of the rebar and to evaluate the efficiency of the treatment to transport both chlorides from the bulk of the mortar to the external anode and nitrites from the cathodic compartment to the level of the rebar. The visual inspection of the rebar shows a free-oxides surface, without any sign of corrosion, confirming the efficiency of the treatment.

The analysis of chloride and nitrite contents confirms the presence of nitrite at the level of the rebar, as resumed in Table 1. High efficiencies of chloride removal are obtained by this method with the rebar connected to the cathode during the treatment: an efficiency of the chloride removal treatment of 75% was reached when the simultaneous application of nitrite was considered, while an efficiency of 55% where obtained with the conventional treatment of chloride removal without simultaneous introduction of nitrite. The presence of NO$_2^-$ at the level of the rebar was also confirmed in a concentration of 0.15% of nitrite by cement weight mass of cement.

Fig. 3. E_{corr} evolution after the disconnection of the electrochemical treatment of chloride removal with and without simultaneous introduction of nitrite as corrosion inhibitor. Rebar connected to the cathode.

Table 1
Analysis of total chloride and nitrite at the level of the rebar after the treatment of chloride removal with connection of the rebar as cathode. Values in % by mass of cement.

Treatment	Rebar connected as cathode	
	% Total Cl$^-$	% NO$_2^-$
Without inhibitor	0.34	–
With inhibitor	0.26	0.15

4. Discussion

During the ECE treatment the rebar is polarized at cathodic potentials associated with the immunity corrosion region of Pourbaix diagram [33]. At this potential both the oxide reduction and the formation of hydroxyl groups by water and oxygen oxidation can be predicted [34]. Then, an increase of the pH near the rebar should be expected. However, high values of corrosion current are often measured when the treatment stops before the new passive state of the rebar is reached days after the treatment [35].

An improvement on the ECE treatment is obtained when the introduction of nitrite by migration from the cathodic compartment to the anodic one is considered. A faster repassivation of the rebar (Fig. 4) takes place probably associated with the anodic inhibitive action of nitrite that could protect the rebar from a further action of residual chloride that could not be eliminated during the treatment. In Fig. 5 has been included the evolution of the cumulative loss of mass estimated from Faraday equation, considering comparison between both treatments, with and without simultaneous migration of nitrite. Lesser losses of mass has been calculated in the case of applying nitrite during ECE treatment, before reaching the new passive state of the rebars after the treatment.

In Fig. 6 a scheme indicating the lines of transport of chloride and nitrite through the concrete during the treatment is included. The transport of nitrite from the ponding located at the external cathode towards the opposed surface of the sample, where is located the anode, is going to be enhanced by the electric field. The transport of chlorides takes place from the bulk of the concrete to the anode. The connection of the rebar to the cathode also favours the electrostatic repulsion of chlorides as well as the water reduction generating hydroxides. These OH$^-$ are going to enhance the alkalinity of the concrete surrounding the rebar and also are going to migrate to the anode in similar way than chloride, decreasing the efficiency of chloride migration.
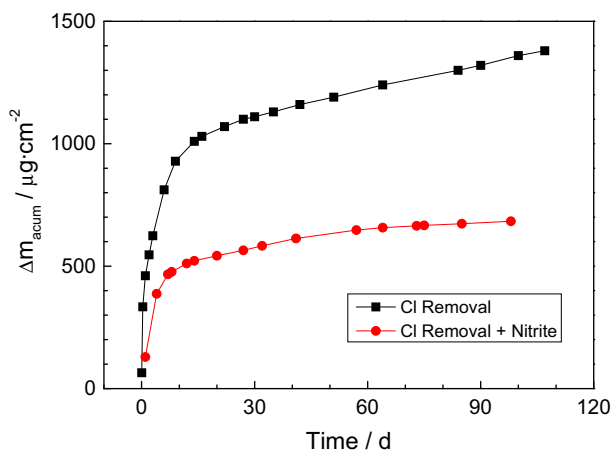

Fig. 6. Transversal section of mortar sample indicating the connections and the lines of transport of chlorides and nitrites.

An homogeneous polarization of the rebar is expected with the arrangement and even though the DC-driving voltage applied during the treatment, no stray current has been detected. Meanwhile stray current effects on the corrosion behaviour of rebar will be observed if the rebars are not connected to the cathode during the application of the electric field between both external electrodes as suggested in [29]. In fact in Fig. 7 corrosion of a rebar after an ECE treatment between two external electrodes without connection of the rebar to the cathode is showed, even though nitrites were also introduced during the treatment.

An heterogeneous distribution of oxides on the rebar surface is observed. The surface of the rebar exposed to the external cathode is drastically affected by corrosion while the other side of the rebar results free-oxide. Then, an analogue response than the stray currents effect can be deduced if an arrangement similar to that of Fig. 8 is used without the connection of the rebar to the cathode if anionic inhibitors want to be introduced during the ECE.

The stray currents generated in this case allow a gradient of potentials between the upper and the lower surface of the rebar, induced by the electric field connected between the external electrodes. The surface faced of the rebar to the external cathode will result polarized to more anodic potentials than the surface faced nearest to the anode. The oxide formation on the rebar surface

Fig. 5. Evolution of cumulative charge registered after each application of treatments for chloride removal with connection of the rebar to the external cathode with and without simultaneous introduction of NO$_2^-$.
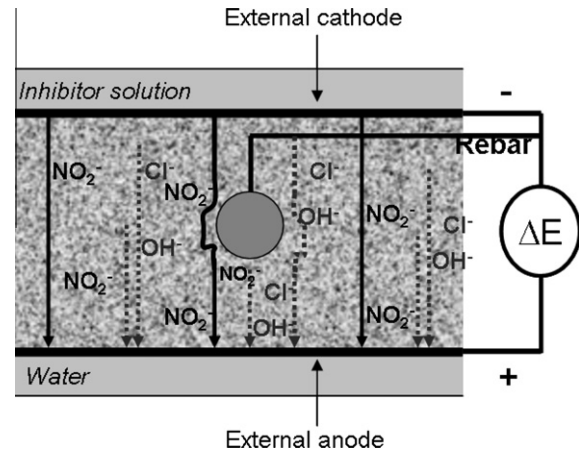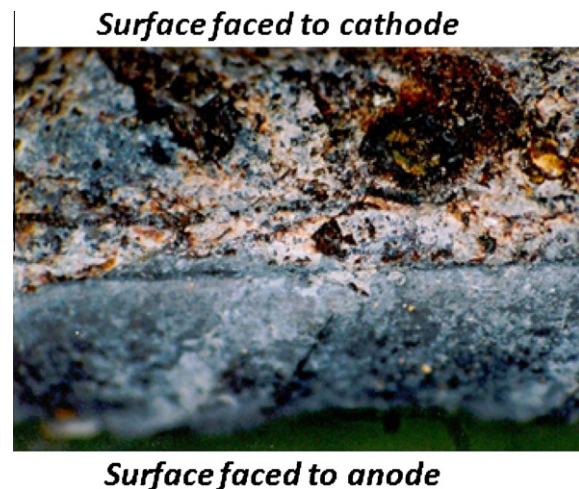

Fig. 7. Visual aspect of rebar after treatment by connection of two external electrodes and with the disconnected. Treatment with simultaneous introduction of calcium nitrite as inhibitor.
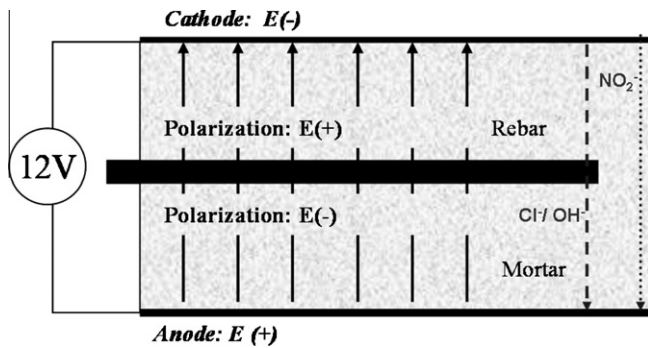
Fig. 8. Solid lines: electric field lines through mortar bulk during connection of two external electrodes with the disconnected rebar located between them. Dash lines: transport of ions through the mortar bulk.

Table 2
Analysis of total chloride and nitrite at the level of the rebar after the treatment of chloride removal (with and without penetration of nitrite). Values in % by mass of cement.

Treatment	Surface faced to cathode		Surface faced to anode	
	% Total Cl^-	% NO_2^-	% Total Cl^-	% NO_2^-
Without inhibitor	0.06	–	0.16	–
With inhibitor	0.14	0.12	0.18	0.36

showed in Fig. 7 supports this hypothesis of higher attraction of Cl^- from the rebar surface faced to the external cathode which has higher potential ($E_1 > E_2$). In this sense, even though the simultaneous penetration of nitrites was considered no improvement of the corrosion response of the rebar was obtained, as the effect was also observed in presence of nitrite, although the transport of nitrite and the removal of chloride were confirmed by analysing the content of these ions in the concrete bulk, as summarised in Table 2. Even though higher concentration of nitrite and lesser concentration of chloride were analysed, the rebar was highly affected by corrosion processes. The effect of the stray currents due to the configuration of the system must control the corrosion response of rebars after the treatment.

This evidence allows emphasising that the rebars have to be connected to the cathode of the electrochemical arrangement used to simultaneously removing of chloride and penetrating of nitrites or anionic inhibitors in the concrete. Although further studies are needed to understand the process of transport of nitrite and the mechanism of passivation of the rebar, the efficiency using an arrangement of two external electrodes and the rebars connected to the external cathode have allowed in present study improving the chloride removal in 35% efficiency, together with the accumulation of nitrites in the surrounding of the rebar ($Cl/NO_2^- = 0.6$) sufficient to allow a faster new passive state of the reinforcement to be reached after the treatment.

5. Conclusions

An efficient arrangement for penetrating nitrite as anionic corrosion inhibitor during an electrochemical treatment of repair with the connection of the rebar to an external cathode is proposed. A 35% higher efficiency of the treatment in chloride removal has been obtained. The presence of nitrite ion at the level of the rebar after the electrochemical treatment has been confirmed in enough quantity to guarantee a quicker and efficient passivation of the rebar that maintains with time.

The penetration of nitrites during a chloride removal using no-connection of the rebar to the cathode favours the presence of stray currents that induced a heterogeneous polarization and further local corrosion.

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