

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

M. Sánchez*, M.C. Alonso

Research Centre of Safety and Durability of Built Structures and Materials – CISDEM (CSIC-UPM), C/Serrano Galvache 4, 28033 Madrid, Spain

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ABSTRACT

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

* Corresponding author. Address: Laboratoire Interfaces et Systemes Electrochimiques (LISE-CNRS), UPMC Case 1334, place Jussieu, 75252 Paris cedex 05, France. Tel.: +33 666875814; fax: +33 1 44 27 40 74.

E-mail addresses: mercesanc@ietcc.csic.es (M. Sánchez), mcalonso@ietcc.csic.es (M.C. Alonso).

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 $\text{Ca}(\text{NO}_2)_2$ 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 $\text{Ca}(\text{NO}_2)_2$ 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], $E_{\text{corr}} < -0.35$ V(SCE) and $i_{\text{corr}} > 0.2$ micro amperes per centimeter square ($\mu\text{A}/\text{cm}^2$). 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.

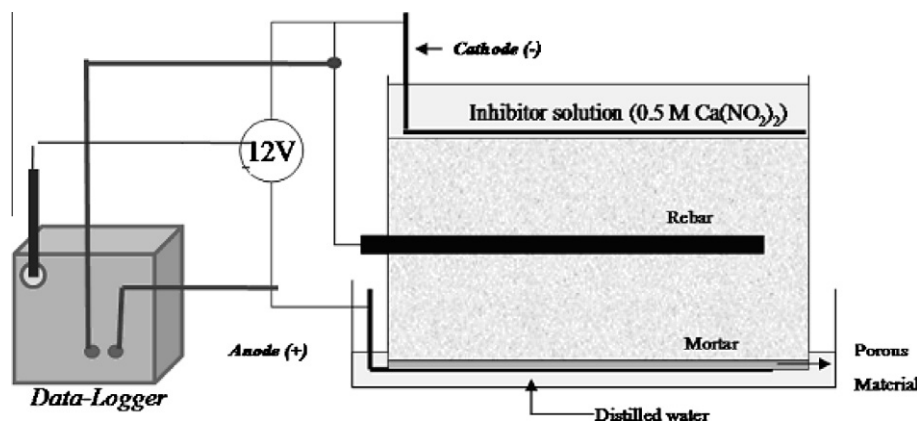


Fig. 1. Scheme of the arrangement for the treatment of electrochemical chloride removal with simultaneous penetration of nitrite.

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