Repassivation of steel rebars after an electrochemical chlorides removal treatment by simultaneous application of calcium nitrite

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ABSTRACT: The Electrochemical Removal of Chlorides (CE) can be proposed as methodology for the treatment of reinforced concrete structures affected by corrosion. This methodology is based on the temporary application of an external voltage between an external anode located on the concrete and the rebar connected as cathode. After the treatment, the extraction of chloride from the concrete level and the repassivation of the rebar are expected. The migration of ionic inhibitors to the rebar could be considered during the connection of an electric field to favour the regeneration of the passive film. In present work a novel methodology is proposed to enhance the efficiency of an Electrochemical Chloride Extraction treatment by simultaneous application of calcium nitrite. A fast repassivation of the rebar is reached after the CE treatment when the inhibitor is applied during the electric field connection. The penetration of the inhibitor near the rebar surface has been confirmed by. The new passive conditions of the steel rebar after the treatment were confirmed by electrochemical measurements. The penetration of the inhibitor near the rebar surface was assured by analysing of nitrite dissolved into the aqueous phase. The presence of nitrite promoted a faster regeneration of the passive film that is maintained in time.

1 INTRODUCTION

In last decades, 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 in the ability of removing the aggressive but maintaining the concrete cover (Polder 2002, Mietz 1998). Three main techniques are distinguished depending on the aggressiveness of the environment and on the type of structure: Cathodic Protection (CP) (Bertolini et al. 1993), Electrochemical Chloride Extraction (CE) (Elsener et al. 1993, Castellote et al. 2000) and Electrochemical Realkalisation (RE) (González et al. 2000, Castellote et al. 2006).

When a reinforced structure is corroding due to the presence of chloride, a temporary Electrochemical Chloride Extraction treatment can be carried out. This methodology aims to extract the chlorides from the concrete bulk by applying an external voltage through an anode located at the surface of the concrete and the rebar connected as cathode (Polder 2002). The connection of the rebar as cathode enhances the formation of hydroxyl ions at the rebar level and then, the alkalinisation of the aqueous phase near the rebar area and the realkalinisation of the carbonated concrete.

By the other hand, the applying of corrosion inhibitors as protective methods on hardened concrete can also be considered. Corrosion inhibitors can be applied on the concrete surface and penetrates dissolved into the aqueous phase of the pores through the concrete cover to the rebar (Page 2000, Elsener 2002). The accelerated transport of inhibitors by migration has been also proposed (Asaro 2000, CSIC-Patent 2001, CSIC-Patent 2008, Swada et al. 2005, Holloway et al. 2004, Sánchez et al. 2008). Then, the simultaneous application of an Electrochemical Repair Technique and accelerated penetration of inhibitors could be expected to promote a synergic effect of both treatments. However, as the rebar is connected

as cathode during the electrochemical repair, only the transport of cationic inhibitors should be considered (Swada et al. 2005, Sánchez et al. 2008).

In present work it is proposed a new novel methodology to enhance the efficiency of an Electrochemical Chloride Extraction treatment by simultaneous application of an anionic inhibitor, as calcium nitrite, that has demonstrated be the most efficient corrosion inhibitor.

2 EXPERIMENTAL PROCEDURE

2.1 *Materials*

The study has been performed on mortar samples fabricated with: CEM I 42.5R/SR resistant to sulphates and with low content of alkalis and aluminates (<4%), normalized CEN UNE-EN 196-1:1196 sand and deionised water. Water/cement ratio of 0.5 and sand/cement ratio of 3/1 have been employed. Sodium Chloride was added to mixing water (1% Cl- by cement weight) to promote the corrosion onset before applying the repair treatment.

Mortar samples of $2 \times 5.5 \times 8$ cm have been fabricated. The mortar specimens were cured in a chamber at $98 \pm 2\%$ of humidity and $21 \pm 2°C$ until the depassivation of the rebar was detected and also after the electrochemical repair treatment had finished. The application of calcium nitrite was considered during the repair treatment by ponding of 0.5 M $Ca(NO_3)_2$ solution on the mortar surface in contact with the external anode.

2.2 *Experimental arrangement*

After the depassivation of the rebar was detected, the electrochemical treatment of chloride removal was applied to repair the corroding samples. The simultaneous application of calcium nitrite as corrosion inhibitor was considered. 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.

During the treatment, a ponding of 0.5 M $Ca(NO_3)_2$ was fixed on the concrete's surface in contact with the external cathode and a continuously humid sponge was 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.

Figure 1 shows the arrangement's scheme for the electrochemical treatment of chloride removal with simultaneous introduction of nitrite as corrosion inhibitor. During the
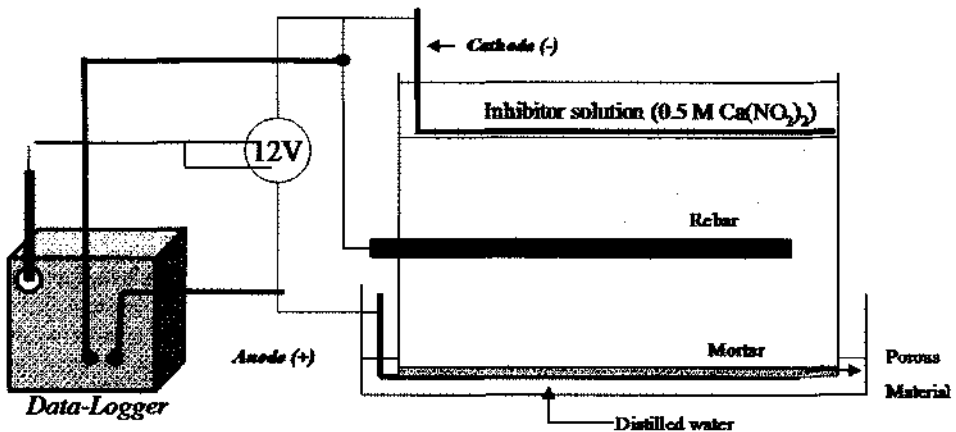

Figure 1. Scheme of the arrangement for the treatment of electrochemical chloride removal with simultaneous penetration of nitrite. (CSIC-patent, 2008).

connection of the electric field the intensity passed through the rebar was monitored with an Agilent Data-Logger*.

The corrosion response of the rebar was analysed before and after the application of the different treatments by measurements of the corrosion potential (E_{corr}). Also the Polarization Resistance (R_p) was periodically obtained for the further estimation of the corrosion current density (i_{corr}). A commercial ACM 1199 Potentiostat* was employed for the electrochemical measurements. At the end of the tests, the sample was broken and a visual observation of the rebar was made in order to confirm its superficial state expected from the electrochemical measurements.

A parallel test without introducing inhibitor was considered as reference, to compare the effect of the presence of nitrites during the treatment. In this case, the ponding with nitrites was replaced with a filled-water one.

3 RESULTS AND DISCUSSION

3.1 *Chloride removal treatment*

The corrosion onset was detected by electrochemical measurements of a rebar embedded into the mortar sample mixed with chlorides and exposed to controlled conditions of relative humidity and temperature ($98 \pm 2\%$ and $21 \pm 2°C$ respectively). The criteria for rebar's depassivation were defined as: values of $E_{corr} < -0.35$ V vs SCE (ASTM C-876-91, 1999) and $i_{corr} > 0.2$ µA · cm^{-2} (COST 521 2003) maintained for 7 days. When the corrosion initiation was detected, the electrochemical chloride removal treatment with simultaneous introduction of calcium nitrite into the mortar sample was carried out.

In Figure 2 the evolution of the current density passed through the rebar during the treatment has been represented. Values of $i \approx 15$ mA · cm^{-2} were measured during the first 3 days of treatment. Then, after 3 days of electric connection, the intensity showed a sharp decay of the intensity to lesser values, below 3 mA · cm^{-2}, that means a decay of more than 75%. These smaller values were maintained along the time of treatment and finally, after 5 days of treatment, the electric field was disconnected.
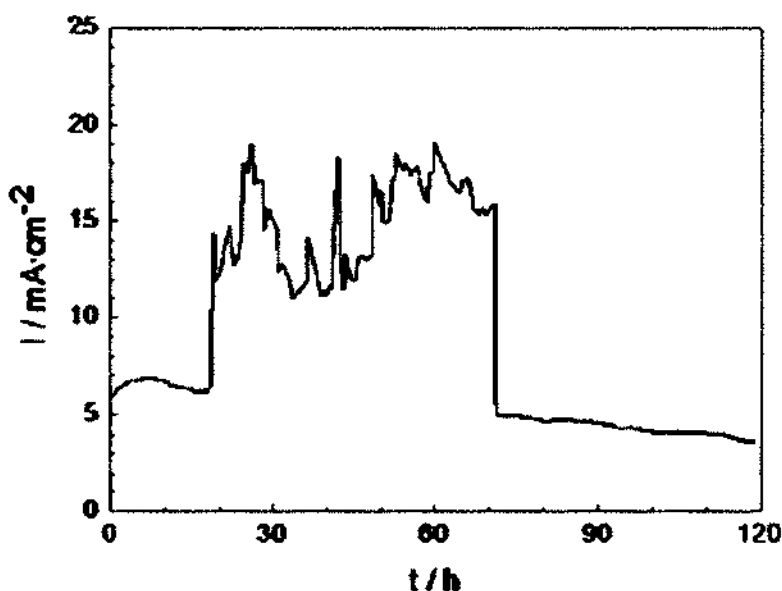

Figure 2. Evolution of the current density passed through the rebar during the treatment of electrochemical chloride removal with simultaneous introduction of nitrite.

3.2 *Electrochemical behaviour after treatment*

After the treatment was finished, the evolution of the electrochemical response of the rebar was monitored to confirm that its repassivation was reached and then, to assure the suitability of the treatment as repair methodology. In Figure 3 the evolution of E_{corr} of the rebar after the treatment with nitrite has been represented. Also the response of a rebar after a treatment of chloride removal without simultaneous application of nitrites has been represented.

Figure 3 shows a faster depolarization of the rebar after the treatment with simultaneous introduction of nitrite than in the case of considering the electrochemical removal of chloride without the application of the inhibitor. The anionic action of the nitrite at the rebar level could enhance the more anodic potentials that are going to favour the regeneration of the passive layer after the electrochemical treatment.

The action of the nitrite enhancing the repassivation of the rebar is also observed from the corrosion current density measurements. In Figure 4 the accumulated corrosion current density of the rebars after the electrochemical treatments has been represented.
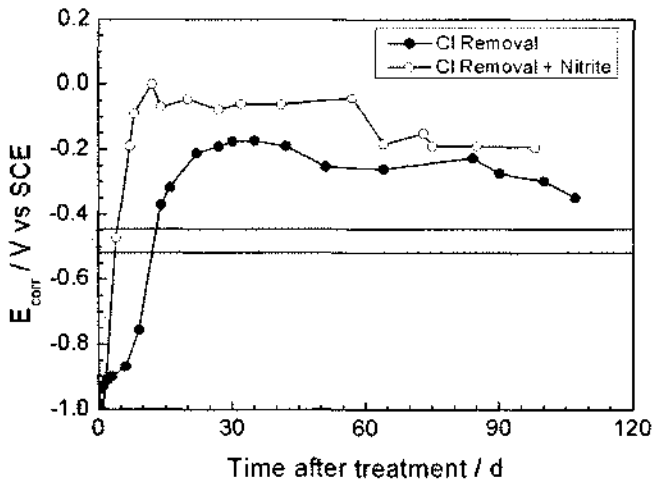

Figure 3.   Evolution of E_{corr} after disconnection of the electrochemical treatment of chloride removal with simultaneous penetration of nitrite as corrosion inhibitor comparing with the treatment without inhibitor.
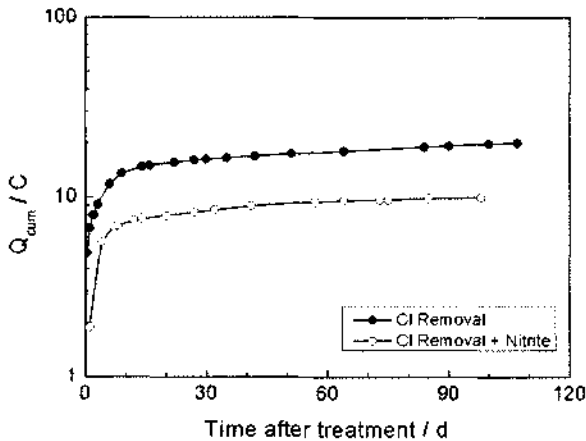

Figure 4.   Evolution of cumulative charge registered after disconnection of electrochemical chloride removal treatments with and without simultaneous introduction of nitrite as corrosion inhibitor.
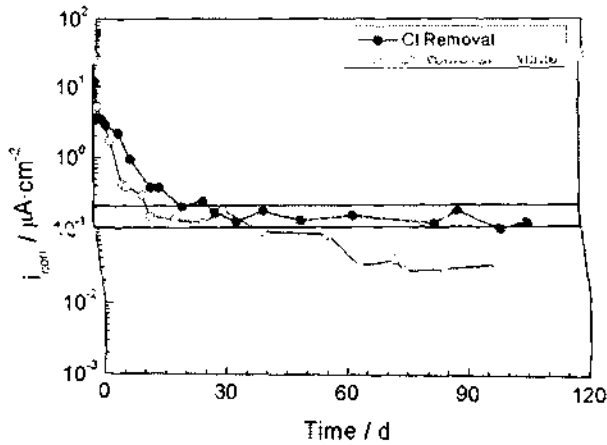
Figure 5. Evolution of i_{corr} after the disconnection of the electrochemical treatment with and without simultaneous penetration of nitrites as corrosion inhibitor.

The inhibitive action of nitrites is associated with the lesser quantity of charge involved in the process of regeneration of the passive film. The nitrite is going to promote a faster formation of protective oxides, associated with the more anodic corrosion potentials and then lesser weight losses are going to be registered when the electrochemical treatment of chlorides removal is carried out with simultaneous penetration of nitrites as corrosion inhibitor.

Also the instantaneous values of i_{corr} measured during 30 days after the electrochemical treatment of chloride removal with simultaneous penetration of nitrite confirms the repassivation of the rebar as can be observed from Figure 5.

During the first 10 days after disconnection high corrosion current densities are registered, indicating a non-equilibrium situation on the system. However, the icorr values decrease with the time of disconnection of the electrochemical treatment and after 10 days of disconnection, values of $i_{corr} < 0.2\ \mu A \cdot cm^{-2}$ indicating a new passive response of the rebar are registered. However, when the simultaneous penetration of nitrite during the electrochemical treatment of chlorides is not considered, a slower decrease on the i_{corr} values is registered, as can be also observed from Figure 5.

3.3 Transport of nitrites to the rebar

After 3 months of the electrochemical treatment disconnection, the mortar samples were broken to confirm the superficial state of the rebars and to evaluate the efficiency of the treatment in transporting both chlorides from the bulk of the mortar to the external anode and nitrites form the catolyte to the level of the rebar. A total chloride concentration of 0.26% of cement weight has been analysed, involving an efficiency of the chloride removal treatment near 75%.

Also the presence of nitrite ions at the level of the rebar was confirmed, $[NO_2^-] \approx 1$ M dissolved into concrete pores. Taking into account the porosity and water content of the pores of the mortar the chloride content can be calculated, giving a ratio $[NO_2^-]/[Cl^-] \approx 0.30$.

The visual inspection of the rebar surface did not show any presence of oxides, confirming in this way the efficiency of the treatment.

4 CONCLUSIONS

An arrangement for penetrating nitrite as anionic corrosion inhibitor during an electrochemical treatment of repair has been presented. The presence of nitrite ion at the level of

the rebar after the electrochemical chloride removal treatment has been confirmed. A ratio $[NO_2^-]/[Cl^-] \approx 0.30$ at the level of the level has been analysed, that seems enough to maintain the system protected during more than 3 months after the disconnection of the treatment.

ACKNOWLEDGEMENTS

REFERENCES

Asaro M.F., Gaynor A.T. & Hettiarachchi. 1990. Electrochemical Chloride Removal and Protection of Concrete Bridge Components (Injection of Synergistic Corrosion Inhibitors). *Strategic Highway Research Program Report SHRP-SIFR-90-002*. National Research Council, Washington DC.

ASTM C-876-91, 1999. *Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete.*

Bertolini L., Bolzoni F., Cigada A., Pastore T. & Pedeferri P. 1993. Cathodic protection of new and old reinforced concrete structures, *Corrosion Science* 35 (5–8): 1633–1639.

Castellote M., Andrade C. & Alonso C. 2000. Electrochemical removal of chlorides—modeling of the extraction, resulting profiles and determination of the efficient time of treatment, *Cement and Concrete Research* 30 (4): 615–621.

Castellote M., Llorente I., Andrade C., Turrillas X., Alonso C. & Campo J. 2006. In-situ monitoring the realkalisation process by neutron diffraction: Electroosmotic flux and portlandite formation, *Cement and Concrete Research* 36 (5): 725–731.

COST 521. Corrosion of steel in reinforced concrete structures. 2003. R. Cigna, C. Andrade, U. Nürnberger, R. Polder, R. Weydert & E. Seitz (Eds). *Final Report. European Communities.* Publication EUR 20599, Luxembourg. p. 82.

CSIC Patent 9801679. 2001. *Procedimiento para introducir especies iónicas o ionizables (orgánicos o inorgánicos) en una estructura de hormigón.* Spain.

CSIC Patent 200803545. 2008. *Dispositivo y procedimiento de uso para la eliminación de agentes agresivos y repasivación de la armadura de un hormigón armado con introducción de inhibidores aniónicos.* Spain.

Elsener B. & Cigna R. 2002. Surface applied inhibitors. In R. Wydert (ed), *COST 521: Corrosion of steel in reinforced concrete structures.* Luxembourg.

Elsener B., Molina M.A. & Böhni H. 1993. Electrochemical removal of chlorides from reinforced concrete, *Corrosion Science* 35 (5–8): 1563–1570.

González J.A., Cobo A., González M.N. & Otero E. 2000. On the effectiveness of realkalization as a rehabilitation method for corroded reinforced concrete structures, *Materials and Corrosion* 51 (8): 97–103.

Holloway L., Nairn K. & Forsyth M. 2004. Concentration monitoring and performance of a migratory corrosion inhibitor in steel reinforced concrete, *Cement and Concrete Research* 34 (8): 1435–1440.

Mietz J. 1998. Electrochemical rehabilitation methods for reinforced concrete structures—a state of the ar report. *EFC Publication No. 24*, European Federation of Corrosion, London.

Page C.L., Ngala V.T. & Page M.M. 2000. Corrosion inhibitors in concrete repair systems, *Magazine of Concrete Research* 52 (1): 25–37.

Polder R.B. 2002. Electrochemical maintenance methods. In R. Wydert (ed), *COST 521: Corrosion of steel in reinforced concrete structures.* Luxembourg.

Swada S., Page C.L., & Page M.M. 2005. Electrochemical injection of organic inhibitors into concrete, *Corrosion Science* 47 (8): 2063–2078.