PULSE CATHODIC PREVENTION – AN EFFICIENT AND COST-EFFECTIVE ELECTROCHEMICAL TECHNIQUE FOR CORROSION CONTROL IN REINFORCED CONCRETE

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Abstract

Cathodic protection (CP) is the only electrochemical technique, able to minimize or stop chloride-induced corrosion in reinforced concrete. The conventional CP, however, has various side effects. This paper discusses a better alternative – pulse cathodic prevention, applied at significantly lower current densities, achieving the required level of protection and expected to exert minimum or none side effects.

Key words: *Cathodic Prevention; Half-cell mapping; Decay; Reinforced concrete*

1. INTRODUCTION

Chloride-induced localized corrosion of reinforcing steel is one of the most hazardous types of corrosion in reinforced concrete [1, 2]. Impressed current cathodic protection (CP) is one of the electrochemical techniques, used for prevention and protection from corrosion in reinforced concrete [3-10]. CP is a well established technique [5, 7], its application, however, is often accompanied by negative side effects (e.g. alkali-silica reaction, bond strength degradation, etc.) [3,7]. Therefore, any improvements of the CP technique, which will minimize the side effects, are an important aspect in corrosion control and corrosion protection of reinforced concrete structures.

This paper presents initial results from an on-going investigation on the performance of cathodic prevention (CPrev) in reinforced mortar and concrete, subjected to aggressive (10% NaCl environment). Cathodic prevention is a technique for minimizing the risk of, actually "preventing", any eventual corrosion of steel in reinforced concrete i.e. the application is before corrosion initiation, using low cathodic current densities (1 to 3 mA/m^2 steel surface). Therefore, the main objective of this investigation is to monitor how efficient is the performance of CPrev in reinforced mortar and concrete as an alternative of CP (preliminary results on reinforced mortar only are reported in [11]. The novelty here is the application of "pulse" CPrev (pulse DC current) instead of the conventional steady DC. The paper reports on generally performed conventional monitoring (i.e. potential mapping and depolarization decay), coupled with microscopic visualization and investigation of the steel/cement paste interface.

2. TECHNICAL BACKGROUND

Impressed current CP is widely used for corrosion protection in reinforced concrete since the 1970's and so far it is proven to be the only technique, able to minimize or stop corrosion in salt contaminated environments [6]. The conventional basis for impressed current CP relies on inducing a negative steel polarization [9, 11] i.e. more cathodic than -850 mV SCE, where corrosion is thermodynamically impossible to occur [13]. When CP is applied to reinforcing steel in concrete however, the objective might not always be to achieve "immunity" but to reduce the risk of chloride-induced corrosion, by polarizing the steel from its condition of chloride-induced corrosion (or "pitting") to the domain of "imperfect passivity", where "pitting" is unstable [6,7,14]. In case CP is initially applied within the construction of a structure, i.e. before exposure to aggressive environments, then only a modest polarization of the steel surface will be sufficient for corrosion protection, the technique being applied and denoted as "cathodic prevention" (hereby discussed and further denoted as "CPrev") [6,15,16].

As aforementioned, there are various side effects, normally accompanying CP applications. A major part of these actually result from microstructural and physico-chemical alterations at the steel/cement paste interface, leading to a reduced adhesion of the cement paste layer to the steel surface [17,18], and thus finally result in bond strength weakening, (the latter reported to reach 55 % [19]). The reason for bond-strength degradation is still unclear, despite the reported data for changes in microstructure, pore size distribution and micro-cracking [17,20,21]. From our previous investigations [22-25] it was found that CP current induces structural alterations in the bulk cementitious matrix, the pore space and the bulk hydration products, causes micro-cracking, which along with softening of the calcium-silica-hydrate (C-S-H) leads to reduced concrete durability, as reported also in [19]. Therefore, a protection regime which uses lower current density (i.e. lower than the usually recommended range of 5 to 20 mA/m^2 for structures exposed to the atmosphere [16]) is expected to minimize the side effects.

In practical applications, the efficiency of a CP technique (CP or CPrev) is generally assessed via monitoring the steel potential with time and decay measurements (ASTMC876 and NACE RP0290-2000). The experimental evidences to support the fundamental principles of CP are very limited [7], but of a significant importance for providing fundamental understanding and prove for the involved phenomena. To this end, previously investigated and reported are CP and pulse CP (pCP) as protection techniques, in terms of a thorough investigation, including fundamental electrochemical monitoring, X-ray methods for steel surface and bulk matrix quali- and quantification, microstructural analysis [25-27]. This work is the first stage of a thorough investigation of CP as a prevention technique i.e. cathodic current applied before corrosion initiation, again as two applications: as steady (CPrev) and pulse (pCPrev) regimes. The contribution aims to prove the applicability and efficiency of the introduced CPrev and pCPrev, evaluated according to standards and via conventional monitoring. Further, SEM and EDX analysis of the steel/cement paste interface provide additional experimental evidence for the fundamental principles of an effectively working cathodic prevention.

3. MATERIALS AND METHODS

3.1. Materials

Two groups of specimens are subject to this contribution: reinforced mortar and reinforced concrete. The "mortar" series was a preliminary work, whereas the "concrete" series is an on-going investigation.

Reinforced mortar: cylinders of h = 150mm, d = 40mm, with embedded "as received" construction steel FeB500 HWL of d=8mm (5 replicates per group and per condition). All specimens used Ordinary Portland cement (OPC) CEM I 42.5, water-to-cement ratio 0.6, cement-to sand ratio 1:3. Curing of the

specimens was performed for 7 days in fog room (20ºC, 98%RH); conditioning was in a laboratory environment (20ºC, lab air) for the total duration of the test of 320 days. The environmental medium was aggressive 10% NaCl solution (specimens were immersed 1/3rd of height for the total duration of the test). In addition to the groups of specimens under both regimes of CPrev, "corroding" and "control" specimens were studied as well.

Reinforce concrete: The steel reinforcement (same as for the "mortar" series: FeB500 HWL, d=12mm, h=200mm) was cast "as received" in concrete cylinders (d=700mm, h=200mm); cement type as for the mortar specimens (CEM I 42.5), casting was according EN 196-1, water-to-cement ratio 0.6 (effective 0.5). Sub-groups of corroding (immersed in 5% NaCl specimens and reference (non-corroding specimens) are also investigated (not hereby commented). Additionally, concrete cubes of 100x100x100 mm were cast from each mixture for standard compressive strength tests (not subject to this discussion). All groups were cured for 28 days in fog room (20ºC and 98% humidity) and then placed in lab conditions: lab air, 22ºC and 1/3rd of height immersed in water or 5% NaCl, 18 replicates per group and condition are monitored.

3.2. Methods

Cathodic Prevention: both CPrev and pCPrev were applied using the conventional way of steady DC cathodic polarization (as in conventional CP applications, where the steel reinforcement is connected to the negative terminal (becoming a cathode) and an inert anode (in this case mixed metal oxide titanium (MMO Ti) is connected to the positive terminal of external power supply). Both mortar and concrete specimens were cast in such a way, that the steel bar was centrally positioned and the MMO Ti anode was embedded in the concrete cover within casting (Fig.1).

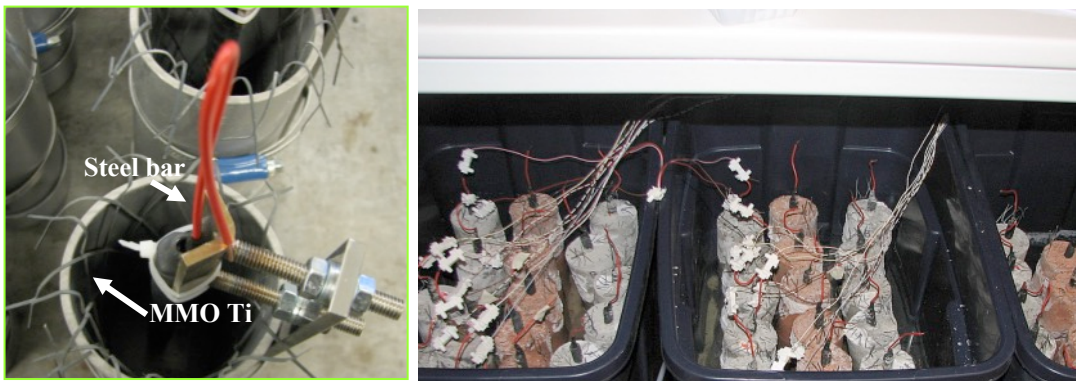


Fig.1. Experimental set-up

Further, the CPrev regime used 1 to 3 mA/m^2 steel surface, whereas the pCPrev regime used effectively 0.5 to 1.5 mA/m^2 i.e. the pulse regime uses 50% of the current density in CPrev regime, since it is applied as a square pulsed DC signal at 12.5% duty cycle and frequency of 1 kHz (the current being the controlling parameter [28]; the pulse regime was previously proven to have superior performance within conventional CP applications [25-27,29,30]).

Experimental methods involved were: Open circuit (OCP) and "on" potentials monitoring for all cells; Depolarization (Decay) measurements; SEM imaging of the steel/cement paste interface for all conditions (using ESEM Philips XL30); EDX analysis; Chemical analysis for total chloride in the vicinity of the steel reinforcement was performed as well, using Volhard titration method.

4. RESULTS AND DISCUSSION

4.1. Conventional monitoring reinforced mortar

The series of reinforced mortar specimens was a preliminary test, started after a shorter curing period (7 days, as previously stated) and in higher aggressiveness of the environmental conditions (10% NaCl) The cathodic polarization started immediately after immersion of the cells in the 10% NaCl solution. The cathodic current density was 1mA per square meter of steel surface and increased to 2.5 mA/m^2 after 90 days. The pulse regime used a block (square) pulse at 1kHz, duty cycle of 12.5% (as previously introduced) and a high impedance current source.

Figure 2 depicts the recorded "on" potentials for both regimes of prevention. As seen from the plot, similar polarization behavior was observed, with potentials reaching -530 mV (SCE) for the steady current CPre and approximately -450 mV (SCE) for the pulse CPre. The current was increased after 90 days (as indicated in the plots) and cathodic polarization increased within the time interval of 320 days, reaching more than -800 mV in cathodic direction for both regimes.

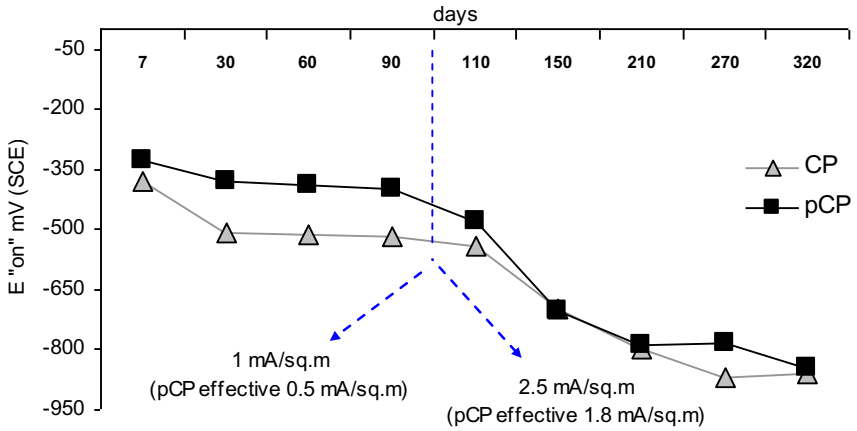


Fig.2 "On" potentials for cells under conventional cathodic and pulse cathodic prevention (the change in current density in time is as indicated in the plot)

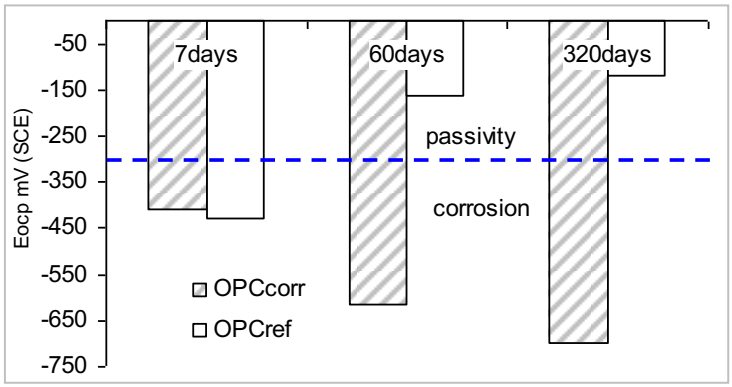


Fig.3 OCP potential readings for "corroding" and "reference" groups in 10% NaCl.

As a comparison (to the "on" potentials), Fig.3 shows the open circuit potential (OCP) readings for corroding and control (reference) specimens OPC corr and OPCref (these are groups without applied cathodic prevention), depicting the passive state of the controls and increased corrosion activity in the corroding cells (according standards, the potential threshold for passive/active behavior of steel in concrete is set as -270 mV vs SCE)

Some considerations with respect to "on" potential readings and decay measurements are necessary to be briefly discussed. As previously introduced, the conventional basis of Cathodic protection is polarizing the steel in the negative (cathodic) direction [1], which is maintaining the steel potential more cathodic than -800 mV (SCE) (BSEN12696). Thus the primary effect is reducing the driving force for the anodic reaction (thermodynamic effect) and retarding the anodic process (kinetic effect). Further, two "protection" processes are expected: a classical thermodynamic immunity or "imperfect passivity", which is a result from restored alkalinity of the environment at the steel/cement paste interface. In that sense, when CP is applied to reinforcing steel in concrete, the objective might not always be to achieve "immunity" i.e. cathodic polarization around -800/-850 mV (SCE), but to reduce the risk of chloride-induced corrosion. This is the domain where CPre actually works, where a modest polarization of the steel surface will be sufficient for corrosion protection. With this respect, the so called "Pedeferri" diagram [6] gives visual correlation of the steel polarization, the involved phenomena and chloride concentration. Therefore, lower polarization (more anodic than -850 mV SCE potential readings) would be sufficient within CPre applications, providing that chloride concentrations are relatively low and most importantly, the decay measurements show sufficient depolarization values. As evident from Fig.2, the initial CPre, both conventional and pulse, result in potential values of about -350 to -500 mV (SCE) for 7 until 30 days of immersion. These fall in the so called "imperfect passivity zone" where pitting can not initiate, although can propagate in the case where corrosion has been previously initiated [6]. The latter case is hereby not relevant, since CPre was applied immediately with immersion in the corrosion medium (for this type of system i.e. specimen geometry and mortar mixture, and for 10% NaCl environment, corrosion initiates after 15 to 30 days after immersion due to chloride penetration and arrival at the steel surface [31]). Further, after 90 days of conditioning, the CP current was increased, and potential readings were more cathodic than -800 mV (SCE) for both pulse and steady CPre regimes.

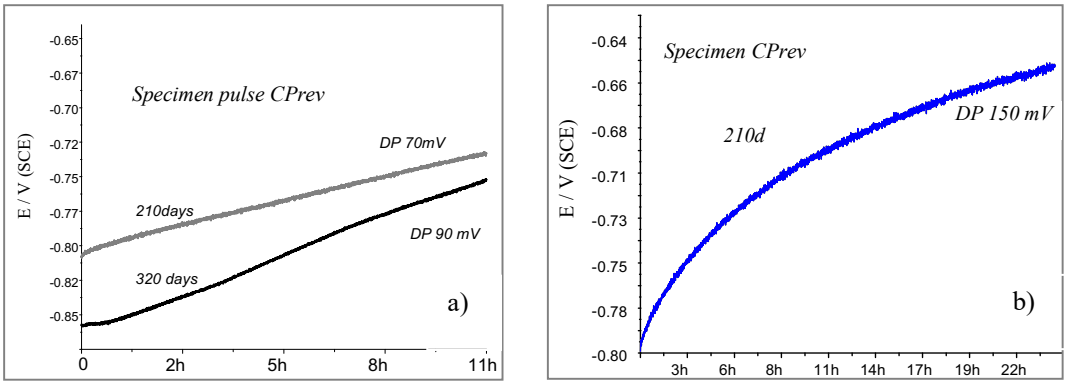


Fig.4 Decay measurements for: (a) mortar specimens under pCPrev (comparison of 210 days and 320 days); (b) mortar specimens under CPrev at 210 days.

Figure 4 depicts the Decay measurements, proving sufficient polarization i.e. the effective prevention in both pulse and steady CPre (according generally accepted criteria, e.g. NACE RP0290-2000, the

decay should be approximately 70 - 100 mV for 24h). Figure 4(a) presents a comparison of decay measurements for mortar specimens under pCPrev as a comparison of 210 and 320 days, showing that the achieved decay is 70 mV at 210 days and 90 mV at 320 days within 11h only (meaning that a sufficient decay of 100 mV will be achieved after 24h). Figure 4(b) depicts a decay measurement for specimens under CPrev, showing a 150 mV decay after 22h. Apparently, both regimes (conventional and pulse) are satisfying the generally accepted (according standards) criteria for protection efficiency.

4.2. Steel/cement paste interface (reinforced mortar at 320 days).

Both CPrev and pCPrev are effectively working according conventional monitoring and accepted criteria. In order to fundamentally prove the latter and moreover, to provide evidence for the performance of both cathodic prevention regimes, the steel/cement paste interface was investigated for morphology, distribution and appearance of product layers (as a result of the different conditions). Additionally, wet chemical analysis was performed for chloride concentrations (total chloride in wt.% per dry cement weight), performed in the locations of interest as shown in Fig.5.

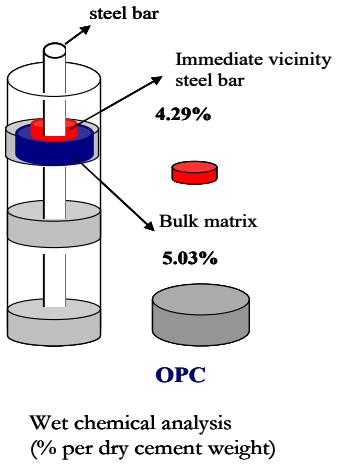


Fig.5 Geometrical location for chloride analysis; the presented values are an average of 3 replicate specimens.

The analysis was performed for all specimens (including those under cathodic prevention). For the corroding specimens and these under CPrev or pCPrev, similar Cl- concentrations were derived: as seen from Fig.5, in both the immediate vicinity of the steel bar, as well as the bulk matrix surrounding the steel surface, chlorides were found to be exceeding the chloride thresholds for corrosion initiation i.e. in the range of 5 wt.%, thus far beyond the threshold of 0.15 wt. % per dry cement weight [10]. Thus, it will be expected that if cathodic prevention was not applied, significant corrosion will be relevant for all specimens. Additionally, it was interesting to know if CPrev indeed halted any corrosion initiation on the steel surface. Therefore, microstructural (SEM) and EDX analysis at the steel/paste interface are essential as evidence of the above. Fig. 6 presents the steel/cement paste interface in a control (Fig.6a) and a corroding (Fig.6b) specimen in comparison with specimens under CPrev (Fig.6c) and pCPrev (Fig.6d).

As seen from the micrographs, there are no corrosion products formed at the interface in the control, CPrev and pCPrev specimens, whereas significant accumulation and already penetration of corrosion products into the bulk cement based matrix is evident for the corroding specimens. Further, EDX

mapping at the steel/paste interface in CPrev (Fig.7a) and pCPrev (Fig.7b) specimens shows none (or minimum) chloride accumulation in the vicinity of the steel surface.

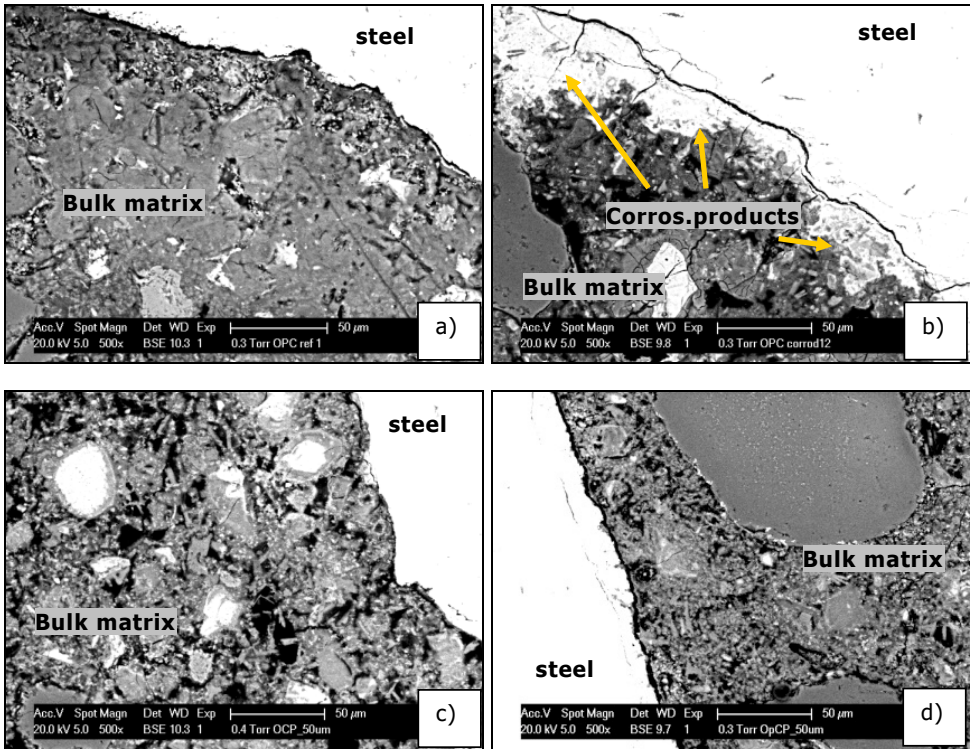


Fig.6 ESEM micrographs (500x) of the steel/cement paste interface in a control (a), corroding (b), CPrev (c) and pCPrev (d) specimens

4.3. Conventional monitoring reinforced concrete

The results from conventional monitoring in reinforced mortar are further correlated with such in reinforced concrete. The "concrete" series is a larger one and is still an on-going investigation. Presented below are the evolution of "on" potentials and decay measurements.

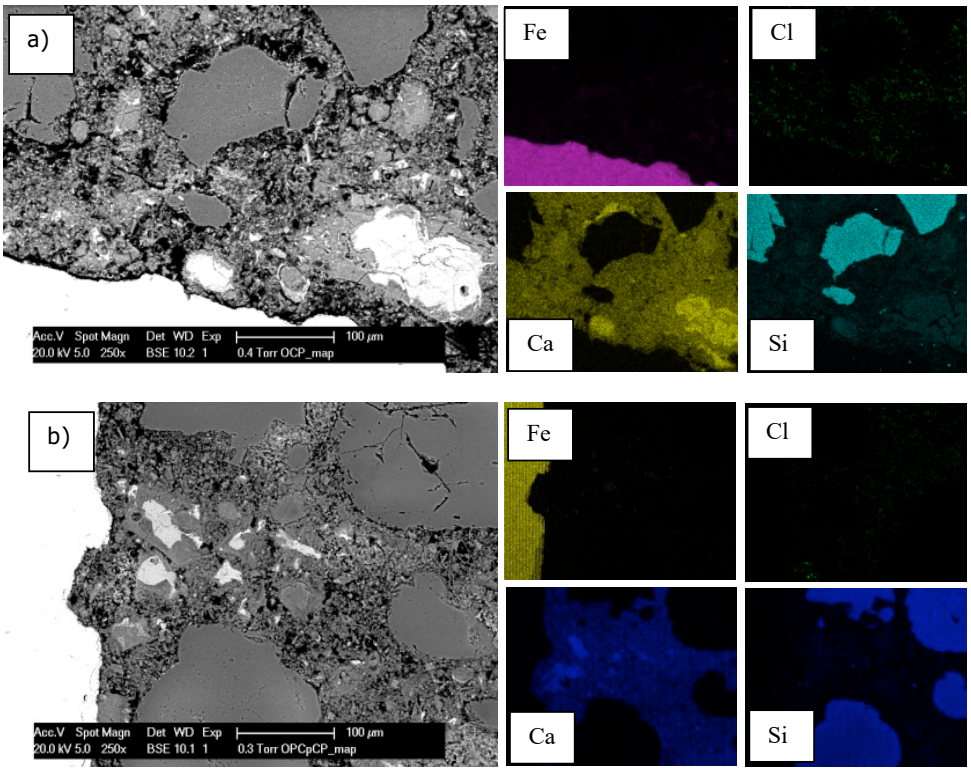


Fig.7 Steel/cement paste interface (left) and the relevant EDX mapping (right) for specimen CPrev (a) and pCPrev (b)

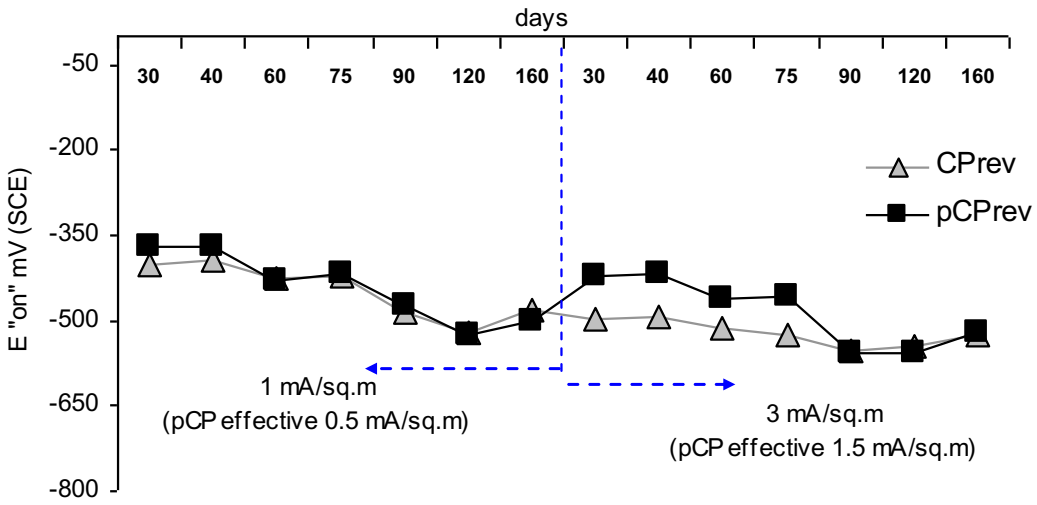


Fig.8 “On” potentials for cells under conventional cathodic (CPrev) and pulse cathodic prevention (pCPrev) (reinforced concrete in 2 regimes of each prevention application: 1 mA/m^2 and 3 mA/m^2 steel surface)

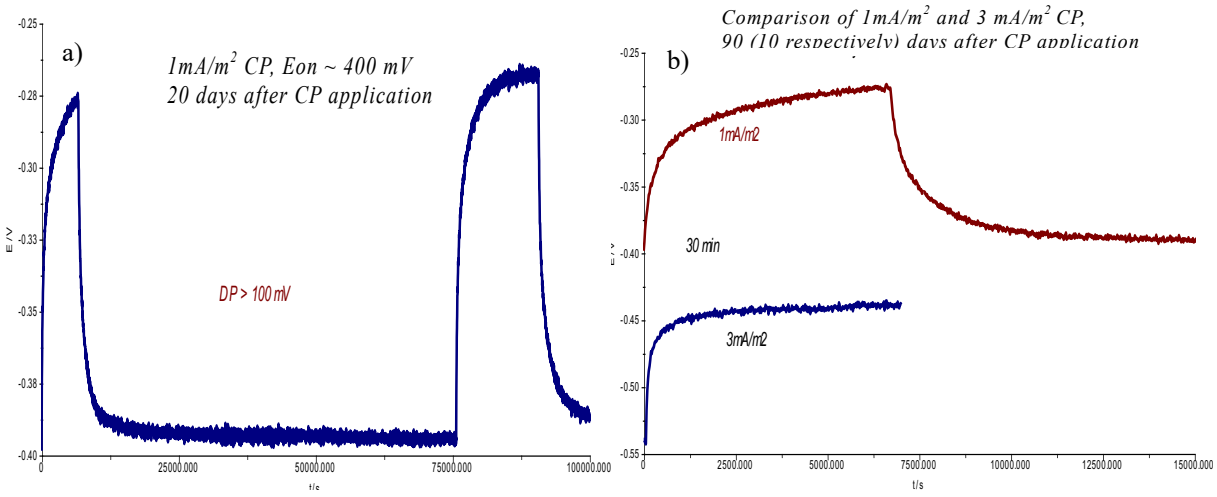


Fig.9 Decay/polarization cycle for specimens under CPrev (1mA.m2) – a); decay/polarization at 1 mA/m^2 and 3 mA/m^2 for specimens CPrev (b)

Fig. 8 depicts the recorded "on" potentials for the CPrev and pCPrev regimes (values are an average of 6 readings i.e. 6 cells per type per age). As seen from the plot, both regimes perform similarly in terms of achieving the relevant polarization (cathodic) and are similar to the previously recorded "on" potentials in mortar (for identical cathodic current densities). The difference here (with respect to mortar) is that the 1 mA current density and the 3 mA current density were applied at same intervals (starting with immersion in 5% NaCl at a concrete age of 28 days). Therefore it can be concluded, that within the application in concrete, there is no significant difference in steel polarization, despite the different cathodic current density values. In other words, the cells under 1mA/m2 behave as those under 3 mA/m2. The result can be only explained with the different microstructural properties (bulk matrix) of the concrete specimens, which were cured for 28 days (in contrast to the previously discussed mortar, cured only 7 days), implying a denser and more matured pore structure and therefore a more closed pore pathways, electrolytic pats and consequently, altered electrical current flow and steel polarization respectively. A correlation of conventional monitoring, electrochemical paramaters and microstructural investigation will be subject to a future work, when the on-going test is finalized.

Further, decay measurements denote for the efficient protection of the steel re-bars, showing sufficient depolarization (of more than 100 mV), Fig.9 (a). A comparison of the decay measurements, resulting form the application of 1mA/m2 and 3mA/m2 (CPrev) is given in Fig.9b). Fig.10 presents the polarization/decay/polarization scans for cells under the pulse regime (pCPrev).

All decay measurements show sufficient steel polarization in both regimes and are in line with the previously recorded behavior for the mortar specimens.

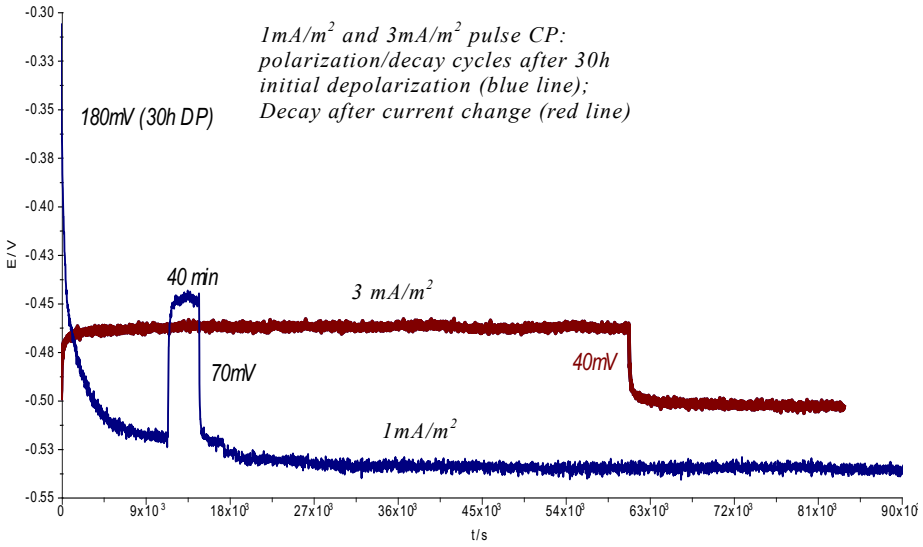


Fig.10 Decay/polarization cycles at 1 mA/m^2 and 3 mA/m^2 for specimens pCPrev.

5. CONCLUSIONS

Both pulse and steady cathodic prevention, using very low current densities (in the range of 1 to 3 mA/m2), are able to prevent corrosion initiation on the steel surface, even in an extremely aggressive environment such as 10% NaCl.

Cathodic polarization was achieved in both reinforced mortar and reinforced concrete specimens, proved by the decay measurements for both groups.

For both CPre and pCPre conditions (mortar series), EDX analysis reveals no corrosion products and minimum (or chemically bound only) chlorides in the immediate vicinity (~ 100 µm away) of the steel/cement paste interface. Chlorides were, however, present in very high concentrations of approximately 5 wt.% in the proximity of the steel re-bars as well as in the bulk matrix, meaning that both regimes of prevention effectively prevented corrosion initiation.

Microstructural changes (mainly in terms of porosity and pore size distribution) are normally accompanying cathodic protection applications. In the case of CP prevention, these changes are expected to be less pronounced. A thorough investigation, including microstructure at the steel/cement paste interface is on-going and will be further reported.

REFERENCES:

1. Hoar T.P, *Corr. Sci*. 1967; 7, 341.

2. Alvarez M.G., Galvele J.R., *Corr. Sci*. 1984; 24, 27.

3. Page C.L., presented at “Concrete Solutions II”, St.Malo, France, 2006, 194.

4. Broomfield J.P., Corrosion of Steel in Concrete, E and FN Spon, London, 1997.

5. Roberts A.C., Glass G.K., Davison N., presented at “Concrete Solutions II”, St.Malo, France, 2006; 295.

6. Pedeferri P., *Constr. Build. Mater*. 1996; 10, 391.

7. Page C.L., Sergi G., *ASCE Journal of Materials in Civil Engineering* 2000; 12, 8.

8. Glass G. K., Green W. K., Chadwick J. R., *Proceedings of Corrosion 91*, Institute of Corrosion, Leighton Buzzard, UK, 1991, 3.

9. BS EN 12696, Cathodic Protection of Steel in Concrete. British Standards Institution, London, 2000.

10. Glass G. K. and. Buenfeld N. R, *Corr. Sci*. 1997, 39; 1001.

11. Koleva D.A., van Breugel K., Mol J.M.C., de Wit J.H.W., Pulse and steady DC Cathodic Prevention of reinforced mortar in chloride environment, 216th Meeting of the Electrochemical Society, Vienna, Austria | October 4 - 9, 2009, Session D1"Corrosion general", paper No 1728, Editor: D. Hansen, publisher The Electrochemical Society, ISSN 1091-8213, www.electrochem.org

12. Bennett J., Turk T., Report No SHRP-S-359, SHRP, Washington D.C. 1994.

13. Pourbaix M., Atlas of Electrochemical Equilibrium in aqueous solutions, NACE, 1996, 312.

14. Pourbaix M., *Corr. Sci*. 1990; 30, 963.

15. Bertolini L., Bolzoni F., Cigada A., Pastore T., Pedeferri P., *Corr. Sci.* 1993; 35, 1633.

16. Bertolini L., Bolzoni F., Pedeferri P., Lazzari L., Pastore T., *J. Appl. Electrochemistry,* 1998; 28, 1321.

17. Ishii K., Seki H., Fukute T., Ikwa K., *Constr. Build. Mat*. 1998; 12, 125.

18. Kuroi T., Sueyoshi T., General Meeting Cement Association of Japan, Tokyo 1987, 164

19. Chang J.J., *Cem. Concr. Res*. 2002; 32, 657.

20. Banfill F.D., "Features of the mechanism of electrolytic re-alkalisation and desalination treatments for reinforced concrete" in Swamy R.N., ed.: Proc. of the Intern.Conference on Corrosion and Protection of Steel in Concrete, 24–28 July, Sheffield, UK, 1994, 1489.

21. Miller J.B., "Structural aspects on high powered electrochemical treatment of reinforced concrete", in Swamy R.N., ed.: Proc. of the Intern. Conference on Corrosion and Protection of Steel in Concrete, 24–28 July, Sheffield, UK, 1994, 1499.

22. Koleva D.A., Hu J., Fraaij A.L.A., van Beek K., Proceedings of Australian Corrosion Association, CAP05, Gold Coast, Australia, 2005.

23. Koleva D.A., van Breugel K., de Wit J.H.W., van Westing E., Copuroglu O., Fraaij A.L.A., *Mater. Character.*, 2008; 59, 290.

24. Koleva D.A., van Breugel K., de Wit J.H.W., van Westing E., Boshkov N., Fraaij A., J. Electrochem.Soc. 2007; 154(3), E45.

25. Koleva D.A., Guo Z., van Breugel K., de Wit J.H.W, *Materials and Corrosion*, 2009; in press doi: 10.1002/maco.200905423

26. Koleva D. A., Guo Z., van Breugel K., de Wit J.H.W., *Materials and Corrosion*, 2009; 60, 704.

27. Koleva D. A., Guo Z., van Breugel K., de Wit J. H.W., *Materials and Corrosion*, 2009; 60, 344

28. EU Patent 05077396.1/EP077395, "Pulse Cathodic Protection of reinforced Concrete", EPO 2005.

29. Koleva D.A., de Wit J.H.W, van Breugel K., van Westing E., Lodhi Z., *J. Electrochem. Soc*., 2007, 154(4), P52

30. Koleva D.A., de Wit J.H.W, Ye G., van Breugel K., Lodhi Z., *J. Electrochem. Soc.* 2007; 154(5), C261

31. Koleva D.A., Copuroglu O., van Breugel K., Ye G., de Wit J.H.W., *Cem. Concr. Comp.,* 2008; 30, 731.