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Anodic behaviour of carbon steel bars in realkalised concrete: potentiodynamic and potentiostatic tests in solution

E. Redaelli, A. Della Pergola, L. Bertolini

Electrochemical realkalisation is a technique used for the repair of reinforced concrete structures suffering carbonation-induced corrosion. It aims at restoring high levels of pH through the application of a temporary cathodic current. Although this technique was introduced in the 1980s and has been used since then, there are still some aspects connected with its application that need investigation. In particular, it is not clear whether the usual techniques for measuring the corrosion activity of steel after the treatment can be considered reliable. This paper presents an experimental study on the anodic potentiodynamic and potentiostatic behaviour of steel in solutions simulating realkalised concrete and, for comparison, in solutions simulating alkaline and carbonated concrete. Results showed that in the alkaline solution used in the treatment steel bars are characterised by passivity, in spite of the high values of corrosion rate measured with linear polarisation technique.

Keywords: Carbonation - Concrete - Concrete simulating solutions - Potentiodynamic anodic polarisation curve - Potentiostatic anodic polarisation - Realkalisation

INTRODUCTION

Although carbonation-induced corrosion of reinforced concrete is often considered easy to cope with, the restoration of structures suffering carbonation is a challenging task that requires the consideration of several requirements. Beside the need to restore the serviceability and safety and to guarantee an adequate durability, it is often required to limit the impact of the intervention on the structure and the environment. Moreover, for artefacts with historical value, the original surfaces should often be preserved. Electrochemical realkalisation (ER) is one of the possible repair methods [1-4]. It aims at restoring high values of pH in concrete through the application of a cathodic current to the reinforcement. Unlike the so called *conventional* repair, ER does not require the replacement of non-protective concrete, allowing to minimise the removal of concrete. Moreover, being a temporary technique it leaves the surface unchanged.
Although ER was introduced in the 1980s and has been used for decades, several aspects connected with its application need investigation. In particular, it is not clear whether the usual techniques for monitoring the corrosion activity of steel after the treatment can be considered reliable. An unexpected increase of the corrosion rate following the application of the treatment has been reported [4-8].
This paper presents the results of a preliminary experimental research on the corrosion behaviour of steel reinforcement in conditions simulating realkalised concrete. Anodic potentiodynamic and potentiostatic tests were performed to characterise the behaviour of carbon steel bars in solutions simulating realkalised concrete, alkaline concrete and carbonated concrete. The results allowed to discuss possible effects of cathodic polarisation on the electrochemical parameters measured after the treatment.

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EXPERIMENTAL METHODS

Electrochemical tests were carried out on steel specimens with various surface conditions, which were immersed in different test solutions. The specimen geometry consisted in a section of ribbed carbon steel bar with length of 80 mm and diameter of 10 mm. All the specimens were sandblasted and the two edges of each specimen were coated with anticorrosion silicon. The length of the exposed surface was 60 mm. The specimens were kept in a desiccator until the beginning of the tests.
Three different solutions were considered: an alkaline solution of NaOH 1M saturated with $Ca(OH)_2$ (pH 13, simulating alkaline concrete), an almost neutral solution of

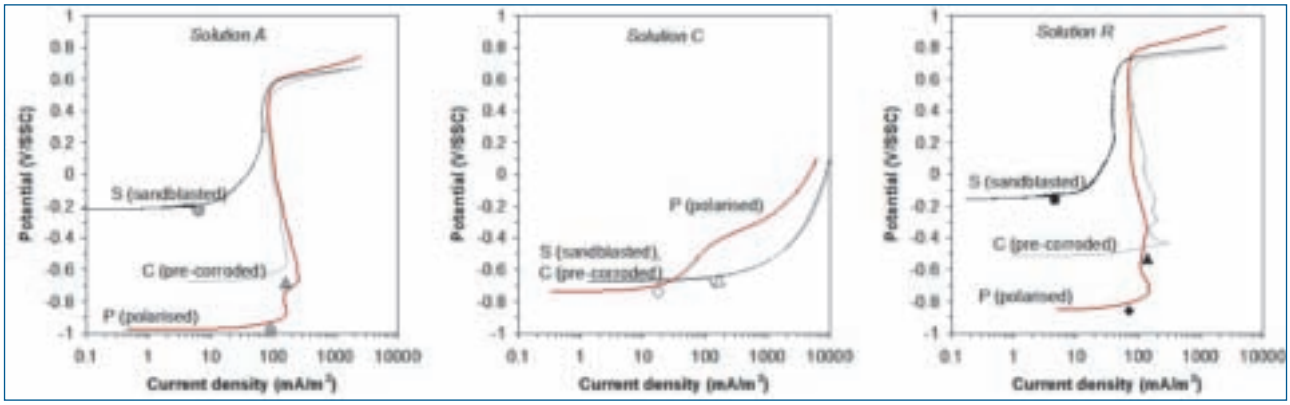

Fig. 1 - Corrosion potential and corrosion rate obtained from LPR tests (symbols) and potentiodynamic curves. Circle = sandblasted (S), triangle = pre-corroded (C), diamond = cathodically polarised (P).

Fig.1 - Potenziale e velocità di corrosione ottenuti dalle prove LPR (simboli) e curve potenziodinamiche. Cerchio = sabbiato (S), triangolo = pre-corroso (C), rombo = polarizzato catodicamente (P).

simple tap water (pH 7.6, simulating carbonated concrete) and a solution of Na_2CO_3 1M (alkaline solution used in ER treatment with pH 11.6 simulating an initially carbonated concrete saturated with such solution); these solutions were indicated with letters *A*, *C* and *R*, respectively. All tests were performed in aerated conditions.

The specimens were tested in three different surface conditions: sandblasted, pre-corroded and cathodically polarised, indicated with letters *S*, *C* and *P*, respectively. Pre-corrosion of steel was obtained by immersing the sandblasted specimens in tap water for 48 hours before the beginning of the test; following this treatment the surface of the specimen was covered by rust. Cathodic polarisation of steel was obtained by applying a cathodic current of 1 A/m^2 for 48 hours to the sandblasted specimens, during immersion in tap water.

Each specimen was positioned in an ASTM-type cell containing 1 L of the test solution. All tests were carried out with an EG&G potentiostat. Silver/silver chloride with saturated KCl solution (SSC) was used as reference electrode, while a carbon graphite bar was used as counterelectrode. All tests were carried out at room temperature and were repeated in triplicate.

A first set of specimens was subjected to potentiodynamic polarisation tests *(PDyn)* preceded by measurement of linear polarisation resistance (*LPR)*. After about 55 minutes from immersion in the test solution, a linear polarisation measurement was carried out by scanning the potential at ±10 mV with respect to the free corrosion potential and recording the circulating current. The scan rate was 10 mV/min. The potentiodynamic anodic polarisation test was carried out on the same specimen in the same solution after 5 additional minutes (i.e. after about an hour since immersion), starting from the free corrosion potential and increasing the potential with a scan rate of 10 mV/min, up to a value of applied current of 5 mA (about 2.6 A/m^2) or a value of potential of 0.1 V/SSC.

A second set of specimens was subjected to potentiostatic polarisation tests *(PStat)*, with the same test arrangement as potentiodynamic tests. After immersion in the test solution, the open circuit potential *(OCP)* was monitored for about 1.5 hours; then, a potential of 0.2 V/SSC was applied for 24 hours, during which the circulating current was measured.

RESULTS

Figure 1 shows the results of linear polarisation resistance and potentiodynamic anodic tests, that were carried out on the first set of specimens; for brevity results of both tests, i.e. open circuit potential and corrosion rate measured with *LPR* after 55 min from immersion in test solution, and anodic polarisation curve measured during *PDdyn*, are reported on the same graph. The scatter of results was very small, so just an example is reported for each test.

In the alkaline solution A sandblasted steel (S) showed a free corrosion potential of –0.22 V/SSC and a corrosion rate of 7.5 mA/m^2. Potentiodynamic polarisation tests indicated a passive behaviour, as highlighted by the presence of a potential range where the current density was roughly constant, followed by an increase in the current at potential values of about 0.5 V/SSC. In the solution C sandblasted steel showed an active behaviour: in free corrosion condition the potential was around –0.67 V/SSC and the corrosion rate 125 mA/m^2. The potentiodynamic curve was characterised by increasing values of current density at increasing anodic polarisation and, at potential values well above free corrosion, the curve was characterised by a linear correlation between potential and current density (in logarithmic scale). In solution R the behaviour of sandblasted steel was very similar to that in solution A, with a free corrosion potential of –0.17 V/SSC, a corrosion rate of 5.4 mA/m^2 and a potentiodynamic curve characterised by a vertical branch up to potential values of about 0.6 V/SSC.

In solutions *A* and *R* the corrosion potentials of pre-corroded specimens *(C)* were –0.62 V/SSC and –0.5 V/SSC

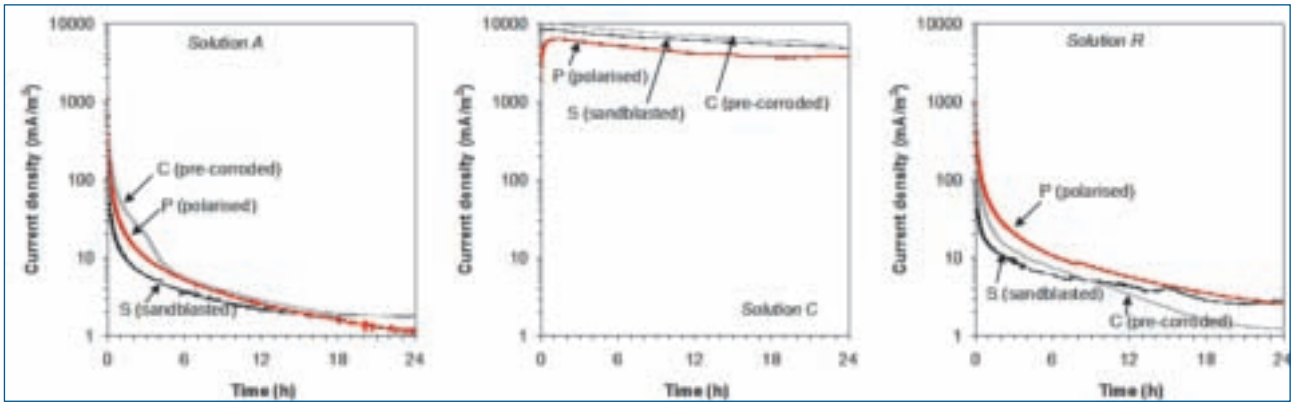

Fig. 2 - Current density during potentiostatic polarisation tests at 0.2 V/SSC.

Fig. 2 - Densità di corrente durante la polarizzazione potenziostatica a 0.2 V/SSC.

(much lower than sandblasted steel) and the corrosion rates were 130 mA/m^2 and 175 mA/m^2 (much higher than sandblasted steel). The potentiodynamic curve showed a similar shape as for sandblasted steel, except for the lower starting potential and for the presence of oscillations of current at potentials just above the initial value. The current density started to increase at potential values around 0.5 V/SSC in solution *A* and 0.7 V/SSC in solution *R*. Pre-corroded steel showed the same behaviour as sandblasted steel in solution *C*, in terms of both free corrosion conditions and shape of potentiodynamic curve.

Cathodically polarised steel (P) showed very negative potential, –0.98 V/SSC, and relatively high corrosion rate, 85 mA/m^2, after immersion in solution *A*. However the polarisation curve showed a large interval of constant or even decreasing values of current density, up to about 0.55 V/SSC. During immersion in solution *C* cathodically polarised specimens showed a potential of about –0.75 V/SSC and a corrosion rate around 25 mA/m^2. The polarisation curve showed an active behaviour, although with a different shape from sandblasted steel due to the presence of a steep rise before reaching a steady slope. In solution R the initial potential was –0.86 V/SSC and corrosion rate 75 mA/m^2, and the polarisation curve showed a large interval of constant current density up to a potential value of 0.75 V/SSC.

Figure 2 shows results of potentiostatic polarisation tests *(PStat)* measured on the second set of specimens, in terms of anodic current density measured during 24 h with an applied steel potential of 0.2 V/SSC. In solution *C*, and for all surface conditions, very high current densities were obtained, of the order of several or ten thousands of mA/m^2. The curves showed a maximum value after 1-2 h and then started decreasing; values after 24 h were lower, but of the same order of magnitude of initial ones, indicating a high anodic activity of steel. In solutions *A* and *R* initial current densities were 10-100 mA/m^2 and the trend with time was continuously decreasing for all surface conditions; values measured after 24 h were one or two orders of magnitude lower than initial values.

DISCUSSION

The results obtained from the tests allow to discuss some aspects related to the corrosion behaviour of steel in contact with solutions simulating an alkaline concrete (alkaline solution *A*), a carbonated concrete (almost neutral solution *C*) and a concrete saturated with a solution of sodium carbonate used in the electrochemical realkalisation treatment (alkaline solution *R*).

Sandblasted steel, which is representative of a clean and non-corroded rebar, showed a passive behaviour when it was in contact with both alkaline solutions; conversely, in the solution simulating carbonated concrete it actively corroded. Pre-corroded steel, which is representative of a rebar that has already undergone considerable corrosion propagation, was passivated by the contact with alkaline solutions. As a matter of fact, the current density remained constant and did not increase up to potential values similar to those obtained for sandblasted steel. When the steel surface was cathodically polarised, oscillations of current density were observed in the polarisation curve, in particular in alkaline solutions. Although no specific analyses were carried out to investigate this aspect, these oscillations can be attributed to concurrent anodic reactions other than iron oxidation. Nevertheless, in alkaline solutions the behaviour was again characterised by passivity and in the neutral solution it was characterised by activity.

On the whole, the potentiodynamic curves shown in Figure 1 highlighted two distinct behaviours that occurred regardless the surface condition of steel: a typical active curve in the solution simulating carbonated concrete, characterised by increasing current, and a typical passive curve in the two alkaline solutions, characterised by intervals of potential where the current remained constant.

The potentiodynamic curves were then quantitatively compared in terms of various parameters characterising the anodic behaviour of steel, such as the current density of the passivity range *(i_p)*, i.e. the current density characterising the vertical branch of the curve, and the transpassivity potential *(E_{trans})*, that defines the upper limit of the

passive behaviour of steel (Table 1). In alkaline solutions i_P was 40-60 mA/m^2 for sandblasted steel, while for pre-corroded and cathodically polarised steel it increased to 75-85 mA/m^2. For all surface conditions, E_{trans} in solution *R* was always about 0.15 V higher compared to that in solution *A*.

Test solution	Surface condition	E_{corr} (V/SSC)	i_{corr} (mA/m^2)	i_P (mA/m^2)	E_{trans} (V/SSC)
A	*S*	–0.222	8	64	0.487
	C	–0.622	134	81	0.485
	P	–0.980	87	81	0.534
C	*S*	–0.673	127	-	-
	C	–0.666	142	-	-
	P	–0.749	26	-	-
R	*S*	–0.172	5	41	0.616
	C	–0.502	176	86	0.705
	P	–0.858	75	76	0.755

Table 1 - Average values of parameters obtained from LPR and PDyn tests.

Tabella 1 - Valori medi dei parametri ottenuti dalle prove LPR e PDyn.

The values of i_P that were obtained with potentiodynamic tests were relatively high, and much higher than the values of corrosion rate expected for passive steel. This may be attributed to the dependence of this parameter on the scan rate of potential: it is well known that increasing the scan rate, increased values of "passivity" currents are obtained [9]. A parameter that is more representative of the real passivity current density can be obtained from potentiostatic tests. Current densities measured after 24 h in both alkaline conditions are of the order of 1-3 mA/m^2 and so indicate a low corrosion activity of steel, regardless the steel surface conditions. Further evidence of the passive behaviour of steel in contact with alkaline solutions comes from the plot of *OCP* potentials on the Pourbaix diagram of steel (Figure 3).

Figure 4 plots the values of steel potential and corrosion rate measured with *LPR* tests. Although they were obtained after a short period of immersion in solution, for sandblasted steel these data reflect the active or passive behaviour obtained from potentiodynamic and potentiostatic tests. For pre-corroded steel, steel potential and corrosion rate were similar to those of actively corroding steel, even in alkaline solutions were a passive behaviour was observed. Cathodically polarised specimens in almost neutral condition showed a lower corrosion rate compared to sandblasted and pre-corroded steel; conversely the corrosion rate was higher when they were exposed to passivating alkaline solutions. This result apparently indicates that cathodic polarisation would not produce any beneficial effect, but rather would result in a higher corrosion activity of steel compared to a non-protective solution. Deeper investigations are needed to explain this phenomenon. However, this result could be related with the increase of the corrosion rate measured with *LPR* technique in concrete after the application of ER treatment (i.e. in a very alkaline environment and following cathodic polarisation). This behaviour was reported by several investigators, particularly following pre-corrosion, and

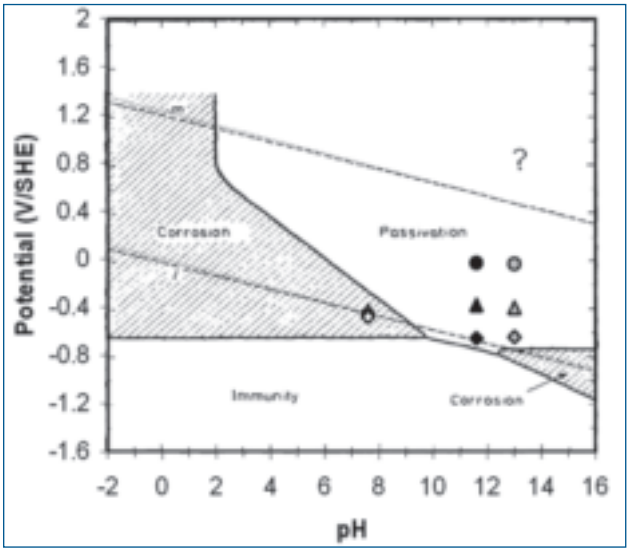

Fig. 3 - Values of OCP measured after 1.5 h of immersion plotted on the Pourbaix diagram of iron in aqueous solutions (modified from [9]). Circles: sandblasted surface; triangles: pre-corroded surface; diamonds: cathodically polarised surface.

Figura 3 Valori OCP misurati dopo 1.5 h di immersione riportati sul diagramma di Pourbaix del ferro in soluzione acquosa (ripreso con modifiche da [9]). Cerchi: superficie sabbiata; triangoli: superficie pre-corrosa; rombi: superficie polarizzata catodicamente.

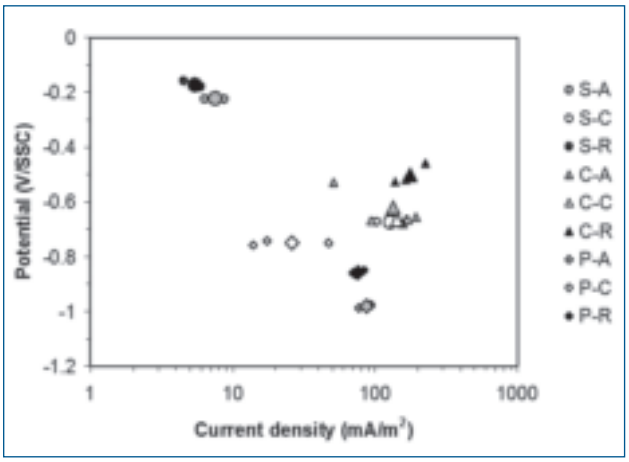

Fig. 4 - Corrosion potential and corrosion current density measured by means of LPR after 55 min of immersion in test solution (big symbols indicate average values).

Fig. 4 - Potenziale e densità di corrente di corrosione misurati con la prova LPR dopo 55 min di immersione nella soluzione di prova (i simboli grandi indicano i valori medi).

its occurrence in concrete-simulating solutions might be exploited to investigate why *LPR* technique overestimates the corrosion rate after cathodic polarisation.

CONCLUSIONS

Alkaline solutions simulating either alkaline concrete or re-alkalised concrete could passivate not only non-corroded steel, but also pre-corroded steel. Passivity current densities obtained from potentiostatic tests at 0.2 V/SSC were as low as 2-3 mA/m^2 and potentiodynamic tests showed that the passivity condition in the polarisation curve was maintained up to potential values of 0.5-0.7 V/SSC.
In an almost neutral solution simulating carbonated concrete, steel bars actively corroded regardless their surface condition. Very high corrosion rates (> 100 mA/m^2) were obtained, except for cathodically polarised steel where lower, but still relatively high, values were obtained (25 mA/m^2).
Both pre-corroded and cathodically polarised steel exposed to alkaline solutions showed corrosion rates after 1-h immersion that were typical of actively corroding steel and not compatible with passive behaviour resulting from other tests. This aspect will be further investigated since it may be related to the high values of corrosion rate obtained with linear polarisation technique in reinforced concrete after application of electrochemical realkalisation treatment.

REFERENCES

[1] J. Mietz, Electrochemical realkalisation for rehabilitation of reinforced concrete structures, Materials and Corrosion, Vol. 46, No. 9, 1995, p. 527-533.
[2] E. Redaelli, M. Carsana, M. Gastaldi, F. Lollini, L. Bertolini, Electrochemical techniques for the repair of reinforced concrete suffering carbonation-induced corrosion, Corrosion Reviews, Vol. 29 No. 5-6, 2011, p. 179-190. DOI: 10.1515/CORRREV.2011.008.
[3] E. Redaelli, L. Bertolini, Electrochemical repair techniques in carbonated concrete. Part I: electrochemical realkalisation, Journal of Applied Electrochemistry, Vol. 41 No. 7, 2011, p. 817-827. DOI: 10.1007/s10800-011-0301-4.
[4] W. Yeih, J.J. Chang, A study on the efficiency of electrochemical realkalisation of carbonated concrete, Construction and Building Materials. Vol. 19, No. 7, 2005, p. 516-524. DOI: 10.1016/j.conbuildmat.2005.01.006.
[5] J. Kubo, S. Sawada, C.L. Page, M.M. Page, Electrochemical inhibitor injection for control of reinforcement corrosion in carbonated concrete, Materials and Corrosion, Vol. 59 No. 2, 2008, p. 107-114. DOI: 10.1002/maco.200804161.
[6] J.A. González, J.M. Miranda, E. Otero, S. Feliu, Effect of electrochemically reactive rust layers on the corrosion of steel in a Ca(OH)2 solution, Corrosion Science, Vol. 49 No. 2, 2007, p. 436-448. DOI: 10.1016/j.corsci.2006.04.014.
[7] J.M. Miranda, J.A. González, A. Cobo, E. Otero, Several questions about electrochemical rehabilitation methods for reinforced concrete structures, Corrosion Science, Vol. 48 No. 8, 2006, p. 2172-2188. DOI: 10.1016/j.corsci.2005.08.014.
[8] D.A. Koleva, Electrochemical behavior of corroded and protected construction steel in cement extract, Materials and Corrosion, Vol. 62 No. 3, 2011, p. 240-251. DOI: 10.1002/maco.200905488.
[9] L.L. Shreir, R.A. Jarman, G.T. Burstein (eds.), Corrosion, Vol. 1, 3rd ed., Butterworth Heinemann, Oxford, 1994.

Comportamento anodico di armature in acciaio al carbonio in calcestruzzo rialcalinizzato: prove potenziodinamiche e potenziostatiche in soluzione

Parole chiave: Acciaio - Corrosione - Caratterizzazione materiali

La rialcalinizzazione elettrochimica è una tecnica di restauro utilizzata per opere in calcestruzzo armato interessate da corrosione da carbonatazione. L'obiettivo è di ripristinare alti valori di pH attraverso l'applicazione temporanea di una corrente catodica all'armatura. Sebbene la rialcalinizzazione elettrochimica sia stata introdotta negli anni '80 del secolo scorso, alcuni aspetti relativi alla sua applicazione non sono ancora stati chiariti. In particolare esistono dubbi sulla attendibilità delle normali tecniche utilizzate per la misura della velocità di corrosione in seguito al trattamento.
Questa nota presenta uno studio sperimentale sul comportamento anodico delle armature in acciaio al carbonio immerse in una soluzione alcalina di carbonato di sodio, rappresentativa del calcestruzzo rialcalinizzato, e, per confronto, in soluzioni neutre e alcaline, rappresentative del calcestruzzo carbonatato e alcalino. Per le armature si sono considerate tre condizioni superficiali: sabbiata, pre-corrosa e polarizzata catodicamente. Sono state effettuate prove potenziodinamiche (PDyn) e potenziostatiche (PStat) anodiche, oltre alla misura del potenziale di corrosione libera (OCP) e della velocità di corrosione con la tecnica della polarizzazione lineare (LPR).
I risultati ottenuti hanno mostrato che le soluzioni alcaline che simulano il calcestruzzo alcalino e rialcalinizzato sono in grado di passivare l'acciaio al carbonio, anche quando è inizialmente fortemente ossidato. Nella soluzione neutra che simula un calcestruzzo carbonatato l'armatura si corrode attivamente indipendentemente dalla sua condizione superficiale.
Infine, sia le armature precorrose sia quelle polarizzate catodicamente, quando immerse in soluzioni alcaline, hanno mostrato velocità di corrosione elevate, non compatibili con il comportamento passivo ottenuto dalle altre prove. Questo aspetto potrebbe essere correlato con gli alti valori di velocità di corrosione che inspiegabilmente si ottengono con la tecnica della polarizzazione lineare su armature in calcestruzzo in seguito al trattamento di rialcalinizzazione.