Durability aspects of electrochemical realkalisation treatment

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ABSTRACT: Electrochemical realkalisation (ER) is a technique used for the repair of concrete suffering carbonation-induced corrosion of steel reinforcement. It aims at restoring high levels of pH through the application of a temporary cathodic current to steel, and subsequent production of alkalinity at the steel surface; a further mechanism of realkalisation relies on the ingress of an alkaline solution in the concrete through the surface in contact with the anode. ER does not require the replacement of carbonated concrete, if it is not damaged, and so it can be advantageous compared to conventional repair, that usually requires the removal of large amounts of mechanically sound concrete. Although ER was introduced in the 1980s and has been used since then for the repair of carbonated structures, there are still some aspects connected with its application that need further investigation. This paper presents the results of an experimental research aimed at investigating the durability of ER, considering both the realkalisation of carbonated mortar and the protection of reinforcement from corrosion.

1 INTRODUCTION

Electrochemical realkalisation (ER) is a repair method for reinforced concrete structures suffering carbonation-induced corrosion (Polder & van den Hondel 1992, Mietz 1998, Bertolini et al. 2013). It aims at restoring high values of pH in concrete through the application of a temporary cathodic current to the reinforcement, that produces alkalinity at the steel surface, combined with the penetration of an alkaline solution (usually sodium carbonate) from the concrete surface. Similarly to other electrochemical techniques, ER does not require the replacement of carbonated concrete, allowing to minimise the removal of sound concrete, which is a laborious and usually undesired operation. Moreover, being a temporary technique it leaves the surface unchanged allowing its application on complex shapes or when the colour and texture of the surface should be preserved. For this reason, it is often considered suitable for fair-faced concrete elements, statues and artifacts with historical, architectural or cultural value (De Jonge 1997).

Although ER has been used as a repair method for carbonated concrete structures for decades, several aspects connected with its application are not fully clear yet. One of these aspects is related to the durability of the effects of the treatment over time, both in terms of keeping in time the alkalinity of concrete and the protection of steel from corrosion.

Literature contributions on the short-term effects of ER are relatively numerous, for instance in terms of the role of several parameters (as concrete composition and circulated charge) on concrete realkalisation and on corrosion conditions of steel reinforcement (Mietz 1995, Redaelli & Bertolini 2011, Tong et al. 2012, Yeih & Chang 2005). Conversely, contributions regarding the long-term effects are few. This note presents the results of experimental research on the long-term behaviour of concrete specimens subject to the treatment. The evolution of concrete realkalisation and corrosion conditions of steel was monitored on mortar specimens subjected to ER treatment and compared to reference carbonated and alkaline specimens.

2 METHODOLOGY

2.1 *Materials*

A mortar (named *A*) was prepared with a portland limestone cement type CEM II/A-LL 42.5R and water/cement ratio of 0.65 (Table 1). Siliceous sand aggregate was used with rounded shape and maximum size of 4 mm. Mortar *A* was used to prepare both plain (i.e. non-reinforced) and reinforced specimens.

Reinforced specimens contained an ordinary carbon steel bar with diameter of 10 mm, that was obtained by cutting segments with length of 160 mm from a ribbed bar. Bars were drilled on one side for electrical connection, then they were sandblasted and kept in desiccator until casting of specimens.

Table 1. Composition of mortar *A* (*w*/*c* = 0.65).

Constituent	dosage kg/m^3
Cement CEM II/A-LL 42.5R	377
Water	245
Sand	1620

2.2 *Specimens*

A total number of 39 specimens were prepared: plain specimens were indicated as A-01 to A-15 and reinforced specimens as A-16 to A-39.

Mortar specimens had dimensions of 40 mm × 40 mm × 160 mm and were used to measure the compressive strength of mortar, to perform absorption tests of the alkaline solution of sodium carbonate (Na_2CO_3 1M) used as anolyte in ER tests and to characterise the resistance to carbonation of the mortar before and after absorption. Reinforced specimens had dimensions of 40 mm × 40 mm × 150 mm and were used to study the corrosion behaviour of steel in alkaline, carbonated and realkalised mortar exposed to an environment with 95% RH and 20°C. Geometric details are shown in Figure 1.

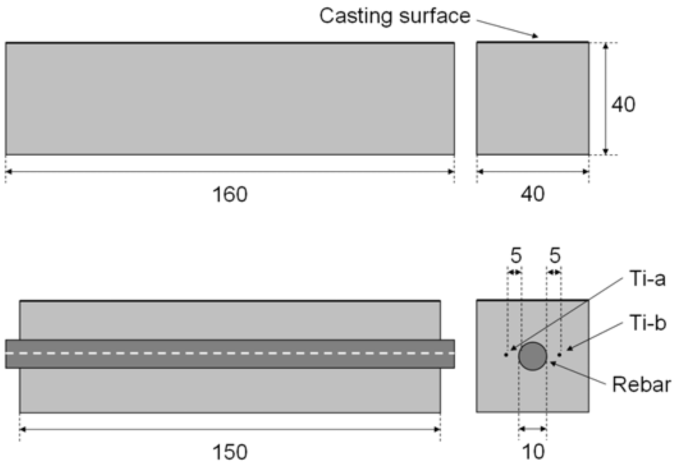

Figure 1. Geometry of plain mortar specimens (*top*) and reinforced mortar specimens (*bottom*). Dimensions in mm.

Each reinforced specimen contained two embedded reference electrodes made with a wire of activated titanium (MMO, mixed metal oxide) that were used to monitor the steel potential and to allow electrochemical measurements. The electrodes were placed parallel to the steel bar at a distance of 5 mm, as indicated in Figure 1, and were indicated as Ti-a and Ti-b. They had the same length of the rebar, but they were isolated so that only a short section (with length of 10 mm), in the middle of the specimen, was in contact with mortar.

All the specimens were de-moulded the day after casting and then wet cured at 98% RH and 20°C for 7 days (except specimens used for compression test that were wet cured for 28 days).

2.3 *Experimental tests*

The mechanical properties of mortar *A* were characterised by measuring the compressive strength after 28 days of wet curing on two specimens. The average value of compressive strength was 29.5 MPa.

The rest of the specimens, which were wet cured for 7 days, were allowed to dry in the laboratory for 7 days and coated with epoxy on mortar or steel bar, if necessary. They were used for different types of tests that will be described in the following.

The resistance to carbonation of initially alkaline mortar was evaluated in accelerated conditions (2% CO_2) and in natural conditions (external environment, sheltered from the rain). The specimens were sealed with epoxy on all sides except one and, after an overall period of 28 days from casting, they were exposed to the carbonation environments. Carbonation depth was evaluated by means of phenolphthalein test (§2.3.1) after various exposure times.

Plain and reinforced specimens that needed to be completely carbonated for the following tests were put in a chamber with 65% RH and 2% CO_2. Two plain specimens were used as sacrificial specimens to check the complete carbonation: when they were completely carbonated (and this occurred after about 40 days), also the rest of the specimens was considered to be carbonated, without any further destructive test. Then, four carbonated plain specimens were used to measure the penetration of alkaline solution of sodium carbonate in the absence of applied current (§2.3.2) and then to measure the resistance to carbonation after the penetration of the alkaline solution, either in accelerated conditions with 2% CO_2 or in natural external conditions. Before exposure to the carbonation environment they were coated on all sides except one. Carbonated reinforced specimens were partly subjected to electrochemical realkalisation treatment (§2.3.4) and partly used as reference to monitor the corrosion conditions of steel in carbonated mortar (§2.3.3). Finally, one reinforced specimen was used for tests of absorption of sodium carbonate, without applied current (§2.3.2).

Alkaline specimens, both plain and reinforced, were used for comparison tests. During carbonation of the previous specimens they were kept in a sealed container to prevent carbonation until the beginning of the tests. Plain specimens were used to measure the penetration of alkaline solution of sodium carbonate in alkaline mortar in the absence of applied current (§2.3.2) and then to accelerated carbonation. Reinforced specimens were subjected to electrochemical realkalisation treatment with duration of 21 days to determine its effects on passive steel embedded in alkaline concrete (§2.3.4). Some specimens were used as reference to monitor the corrosion conditions of steel in alkaline mortar (§2.3.3).

Selected reinforced specimens (realkalised and reference) were used for anodic potentiostatic tests (§2.3.5).

In the following, details of experimental procedures are described. The realkalisation tests, either by absorption of alkaline solution or application of cathodic current, were performed in parallel; before and after realkalisation tests, all specimens were conditioned at 95% RH.

2.3.1 *Measurement of carbonation/realkalisation*

pH indicators were used to detect the advancement of carbonation or realkalisation. Phenolphthalein indicator (that has a pH transition around 9) and a universal indicator based on thymolphthalein (that has a range of colours as a function of pH, in particular it turns dark blue for pH higher than 12) were sprayed on the freshly broken or cut surface of mortar, and the colour distribution on the surface was observed.

2.3.2 *Absorption tests with alkaline solution*

Tests of absorption of alkaline solution, without any applied current, were carried out on carbonated and alkaline specimens and, in addition, on one carbonated reinforced specimen. The specimens were placed over a layer of cellulose pulp soaked with a solution of Na_2CO_3 1M for 21 days (Fig. 2). The mass of each specimen was measured daily; in addition, after 7, 14 and 21 days some specimens were broken and fracture surfaces were sprayed with phenolphthalein and commercial pH indicators to determine the alkalinity of the mortar.

Figure 2. View of specimens during absorption test with alkaline solution of Na_2CO_3 1M.

2.3.3 *Monitoring of corrosion conditions of steel*

Steel potential was measured versus the internal reference electrode Ti-a, that was calibrated versus an external reference electrode (silver/silver chloride, SSC, placed on the cast surface). Corrosion rate was measured with linear polarization technique, by applying a potential of ±10 mV with respect to the free corrosion potential and measuring the circulating current after 30 s.

2.3.4 *Application of ER treatment*

Electrochemical realkalisation treatment was applied with a cathodic current density of 0.5 A/m^2 referred to steel surface. This relatively low value was selected to highlight realkalisation fronts over the mortar thickness of 15 mm. Treatment durations of 7 (ER 7d), 14 (ER 14d) and 21 (ER 21d) days were considered, that correspond to circulated charge densities of 84, 168 and 252 $A \cdot h/m^2$, respectively. Each specimen was placed over a layer of cellulose pulp soaked with a solution of Na_2CO_3 1M containing an activated titanium mesh as anode (Fig. 3). The cast surface of each specimen was placed laterally, so that Ti-b was at the bottom (close to the anode) and Ti-a was at the top. During the treatment the applied current, feeding voltage and steel potential were monitored with on-off techniques. After interruption of the treatment, some specimens were cut to measure realkalisation.

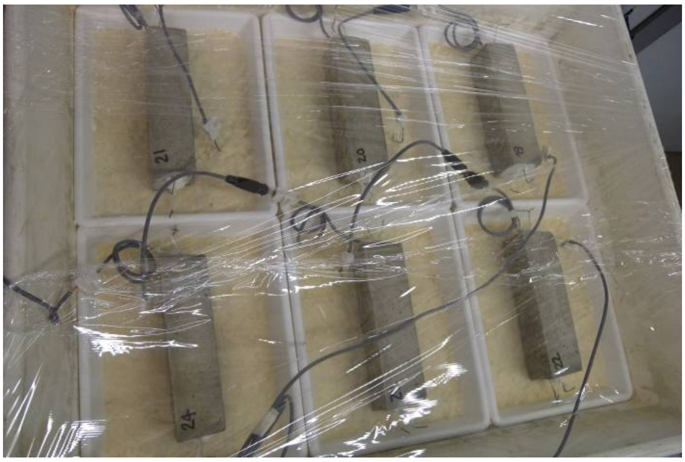

Figure 3. View of specimens during ER test.

2.3.5 *Anodic potentiostatic test*

Anodic potentiostatic tests were carried out by applying a potential of +150 mV/SSC to steel reinforcement and measuring the circulating current for a period of 24 h. Potentiostatic tests were carried out on reference specimens and on specimens subject to ER either immediately after the end of the treatment (i.e. about a week after the interruption of the current) or several months later, to investigate the evolution of corrosion conditions of steel.

3 RESULTS AND DISCUSSION

3.1 *Evolution of realkalisation*

The comparison between realkalisation due to simple absorption of alkaline solution of sodium carbonate (evaluated on plain specimens) and realkalisation due to applied current (evaluated on reinforced specimens) was previously discussed in Bertolini et al. (2012), and is shortly summarised here. Figure 4 shows an example of the alkalinity profiles of initially carbonated mortar after 7, 14 and 21 days of absorption of alkaline solution. All specimens showed a high penetration of solution close to the cast surface, that led to an irregular penetration front. This result can be attributed to the higher porosity of mortar in this area compared to the rest of the specimen due to bleeding phenomena (during casting of the specimens this surface was oriented upwards). Hence, the amount of realkalisation was evaluated as the fraction of the surface area with pH higher than 9: average values of 38.7% (7 days), 47.7% (14 days) and 55.9% (21 days) were obtained (Table 2). These results indicate that the realkalisation of a relatively porous mortar with *w*/*c* ratio of 0.65 by the simple contact with the alkaline solution of sodium carbonate does not exceed a depth of few tens of millimetres.

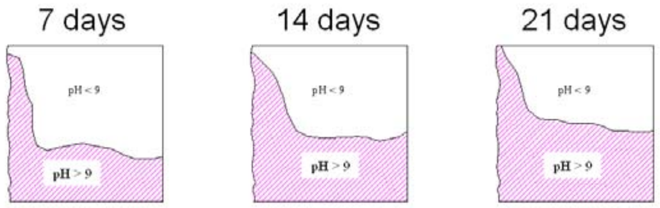

Figure 4. Evolution of mortar realkalisation on an initially carbonated specimen subject to absorption of alkaline solution of Na_2CO_3 1M. Penetration of solution through bottom side; left side (irregular) represents cast surface.

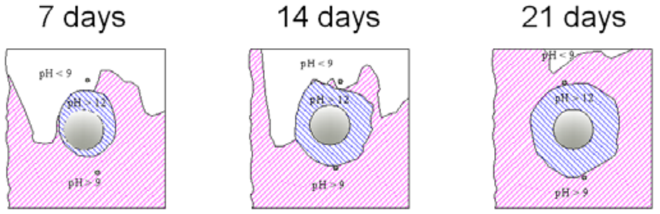

Figure 5. Evolution of mortar realkalisation on an initially carbonated reinforced specimen subject to ER treatment. Anodic system at the bottom side; left side (irregular) represents cast surface.

Figure 5 shows an example of the evolution of realkalisation of an initially carbonated specimen subject to ER treatment. Overlapping results obtained with phenolphthalein and commercial indicator allowed to distinguish areas with pH lower than 9, between 9 and 12, and higher than 12. Average values of the percentage of realkalised surface are reported in Table 2. The realkalised area with pH higher than 9 is considerably higher compared to results from simple absorption tests: 54.6% after 7 days, 72.1% after 14 days and 96.5% after 21 days. Even neglecting the areas with pH higher than 12 (that are certainly due to the cathodic reaction, since the pH of the alkaline solution is around 10.5) and considering only areas with pH between 9 and 12 (that can be attributed to the penetration of the alkaline solution), values of 45.4% (7 days), 55.9% (14 days) and 74.7% (21 days) are obtained, which are higher than those obtained in simple absorption. This suggests that the applied cathodic current contributes to the realkalisation process not only through the cathodic reaction at the steel surface, but also through the promotion of the ingress of the alkaline solution.

Table 2. Average amount of realkalised area evaluated on plain specimens subject to absorption of alkaline solution of sodium carbonate and reinforced specimens subject to *ER* treatment.

	7 days	14 days	21 days
Absorption			
pH > 9	38.7%	47.7%	55.9%
ER treatment			
pH > 9	54.6%	72.1%	95.6%
pH > 12	9.3%	16.2%	21.8%
9 < pH < 12	45.4%	55.9%	74.7%

3.2 *Resistance to re-carbonation*

Results shown in the previous section indicate that at the end of the realkalisation treatment both plain and reinforced specimens underwent penetration of the alkaline solution of sodium carbonate and a front of realkalised mortar of at least 15 mm was detected.

The resistance to carbonation of the specimens after realkalisation was evaluated on plain specimens, both in accelerated and natural conditions, and it was compared with that initially measured on alkaline specimens. Results are shown in Table 3.

After 28 days of exposure to 2% CO_2, initially alkaline mortar showed a depth of penetration of 15 mm. After realkalisation, mortar in the same exposure condition showed a negligible depth of carbonation (1.5 mm). Alkaline specimens that were subjected to absorption of the alkaline solution also showed a negligible carbonation depth.

Table 3. Average depth of carbonation measured with phenolphthalein tests on plain specimens before and after absorption of the alkaline solution of sodium carbonate (slash separates replicate values).

	Carbonation depth
	mm
Initially alkaline mortar	
Accel. (2% CO_2), 28 days	13/17
Natural (ext. sheltered), 28 days	0/0
Natural (ext. sheltered), 1 year	6/7
Natural (ext. sheltered), 4.7 year	10/12
After penetration of sodium carbonate	
Accel. (2% CO_2), 28 days	0/3
Accel. (2% CO_2), 28 days*	0/0
Natural (ext. sheltered), 28 days	0/1
Natural (ext. sheltered), 3.7 year	>23**

* Alkaline specimens that were not carbonated before absorption of alkaline solution.

** Depth of realkalisation at the end of absorption treatment.

In natural conditions of carbonation, initially alkaline mortar showed depth of carbonation of 6-7 mm after 1 year and 10-12 mm after almost five years. Realkalised mortar showed an almost completely carbonated surface after about four years of exposure, in spite of the alleged buffer effect of the solution of sodium carbonate. It seems that in this case the alkalinity reached through penetration of alkaline solution was more ephemeral compared to that of a sound, non-carbonated mortar. Hence, a discrepancy emerged between results of accelerated tests, that indicate a beneficial effect of the alkaline solution in delaying re-carbonation, and results of long-term tests in natural conditions, that seem to suggest that this effect may vanish on the long term in terms of contribution to protection from future carbonation.

3.3 *Corrosion conditions of steel*

The effectiveness of the electrochemical realkalisation treatment in stopping reinforcement corrosion was investigated by monitoring the corrosion conditions of steel in realkalised specimens and comparing with reference specimens, in a wet environment where the propagation of corrosion on active steel is promoted.

Figure 6 shows an example of the trends of potential on specimens subject to ER treatment with different durations (instant off values of potential measured during the treatment are also reported). Before the treatment potential values were between –200 and –400 mV/SSC for all the specimens; these values are representative of active corrosion in carbonated concrete in moist conditions. After the treatment, no substantial changes in potential occurred for the specimens treated for 7 days, while a significant increase in potential was observed on specimens treated for 14 and 21 days. The increase of the free corrosion potential after the application of the treatment is often taken as indication of steel repassivation. Figure 7 shows the trends of corrosion rate measured with the linear polarisation technique on the same specimens. The corrosion rate decreased with increasing treatment duration from values higher than 10 mA/m^2 (much higher than those measured on the same specimen before the treatment) to values of about 2 mA/m^2.

Figures 8-9 summarise the free corrosion potential and corrosion rate for all the conditions considered. In initially carbonated specimens a progressive increase in potential by increasing the treatment duration was observed. However, values measured after 21 days of treatment were still lower compared to passive steel in alkaline concrete. This occurred even for the alkaline specimen that was subjected to the ER treatment for 21 days. For the corrosion rate a similar trend with the treatment duration was observed, since the corrosion rate decreased by increasing the treatment duration, however the values were higher compared not only to passive steel, but also to active steel in carbonated concrete. This apparent detrimental effect of the treatment is in contrast with the expected beneficial effects of an applied cathodic current.

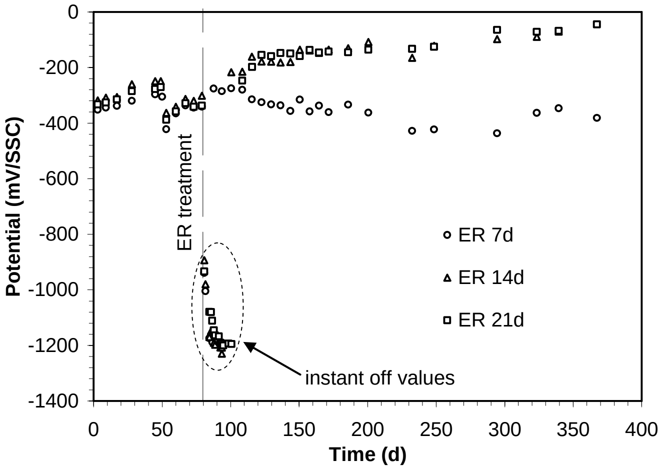

Figure 6. Free corrosion potential of steel of carbonated specimens subjected to ER treatment with various durations, during exposure to 95% RH.

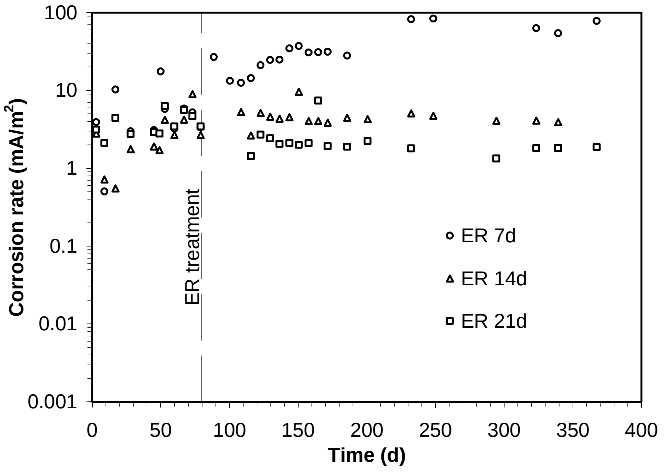

Figure 7. Corrosion rate of steel of carbonated specimens subjected to ER treatment with various durations, during exposure to 95% RH.

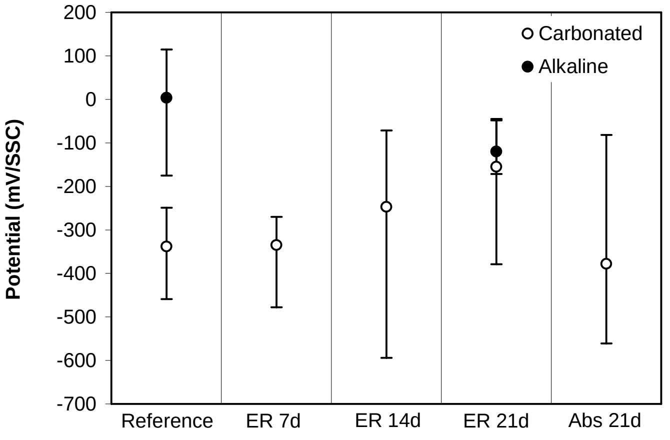

Figure 8. Free corrosion potential of steel during exposure to 95% RH on reference specimens and realkalised specimens.

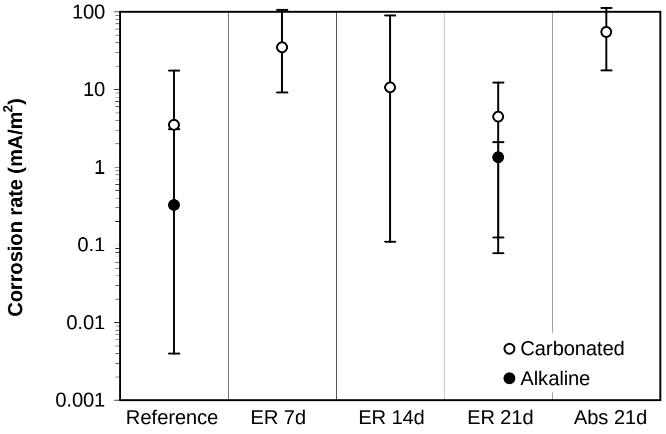

Figure 9. Corrosion rate of steel during exposure to 95% RH on reference specimens and realkalised specimens.

This aspect was further investigated through potentiostatic anodic tests: Figure 10 shows examples of current densities measured during application of a potential of +150 mV/SSC to steel for 24 h. At this potential, if the steel is passive and in contact with alkaline concrete, the circulating anodic current density would be roughly the passivity current density, i.e. a negligible value, as it was obtained for the alkaline reference specimens that showed values of current density always lower than 0.1 mA/m^2. In carbonated concrete the current density was very high, around 100-1000 mA/m^2: such values are representative of active steel. Realkalised specimens showed two distinct behaviours: those with treatment duration of 7 days or with simple absorption of alkaline solution showed values of anodic current density of 100 mA/m^2 or higher, whilst those with treatment duration of 14 or 21 days showed values around 1 mA/m^2, much lower than the previous ones although still higher than passive steel.

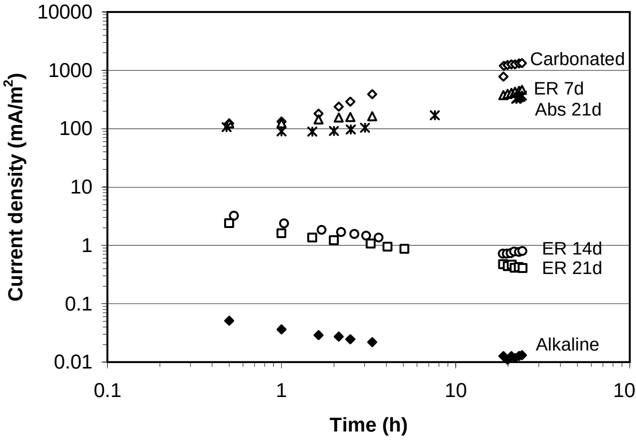

Figure 10. Anodic current density measured on steel during 24 h of polarisation at +150 mV/SSC on reference specimens and realkalised specimens.

Results of potentiostatic anodic tests are summarised in Figure 11 that shows the final value of anodic current density measured after 24 h (multiple values refer to tests repeated at several times on the same specimen). The anodic current density on specimens subjected to ER treatment was progressively decreasing with the treatment duration and it was always lower compared to carbonated reference condition. Considering the anodic current density measured during potentiostatic tests as a measure of the anodic activity of steel, these results are more consistent with the expected progressive beneficial effect of the applied cathodic current in terms of protection of steel from corrosion. Conversely, corrosion rate measured with the linear polarization resistance technique may not be reliable, as it was reported by several authors (Kubo et al. 2008, González et al. 2007). However, comparing results shown in Figure 11 with the realkalisation pattern obtained with pH indicators, it is evident that the detection of a realkalised layer around the steel cannot guarantee by itself the achievement of protection from corrosion, since the corrosion activity of steel can still be relatively high. As a matter of fact, the corrosion activity of steel after 7 days of ER treatment was comparable to that in carbonated concrete, although a layer with pH higher than 12 was detected around the steel bar (Fig. 5).

Finally, Figures 10-11 also suggest that it is unlikely that mortar realkalisation due to the simple absorption of alkaline solution can fully protect steel from corrosion, as indicated by the high corrosion activity of steel highlighted by potentiostatic tests on the reinforced specimen subject to absorption test (Figs. 10-11).

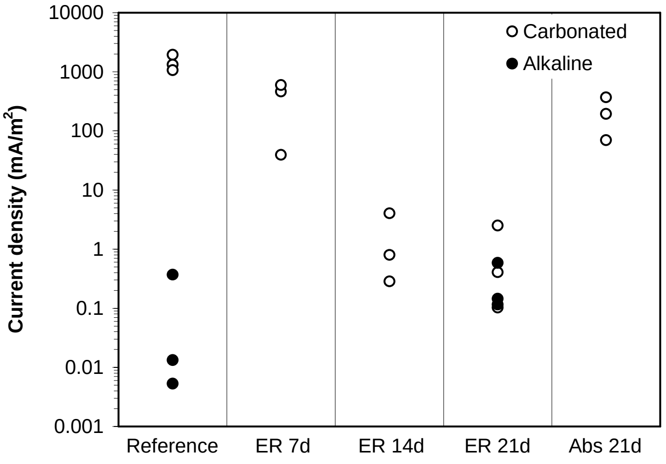

Figure 11. Anodic current density measured on steel after 24 h of polarisation at +150 mV/SSC on reference specimens and realkalised specimens.

4 CONCLUSIONS

The cathodic current applied during ER treatment contributes to the realkalisation process not only through the production of alkalinity at steel surface but also through the promotion of the ingress of the alkaline solution of sodium carbonate.

The ingress of the alkaline solution by itself, through a mechanism of simple absorption, seems unsuitable to provide a durable protection neither in relation to future carbonation of mortar, nor in relation to the protection of steel from corrosion.

The effectiveness of ER treatment cannot be assessed only through pH analyses, since the detection of areas with high pH close to steel surface may not be representative of protection conditions for steel. However, even the measurement of electrochemical parameters can be misleading; in particular, high values of corrosion rate can be detected after treatment. Although it is unlikely that a treatment with short duration may have a detrimental effect on steel, an incomplete protection may result in a high corrosion activity, comparable to that in reference carbonated condition.

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