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ORIGINAL PAPER

Electrochemical repair techniques in carbonated concrete. Part I: electrochemical realkalisation

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Abstract Corrosion induced by concrete carbonation can be controlled through the application of electrochemical techniques such as cathodic protection (CP) or electrochemical realkalisation (ER). These methods are generally considered effective in the repair of structures; however, few data are available on the effects of different parameters such as the concrete composition or the exposure conditions. For the temporary technique of ER, moreover, scarce information exists on the durability of the treatment. An experimental research was carried out, aimed at investigating some aspects connected with the application of these techniques in reinforced carbonated concrete. Six different types of concrete mixes were considered. The tests were performed both in a wet and a dry environment. The effect of the pre-corrosion of the reinforcement in concrete was also considered. This article presents results obtained with the technique of ER and discusses the role of the different factors considered. The technique of CP will be discussed in Part II.

Keywords Corrosion · Concrete · Carbonation · Realkalisation · Repair

1 Introduction

Corrosion of reinforcement due to concrete carbonation is one of the most common causes of damage of concrete structures operating in atmospheric environments. Concrete carbonation is a natural process in which the carbon dioxide present in the atmosphere reacts with the alkaline compounds present in the concrete, neutralising them. The carbonation process occurs from the outermost layers of concrete and progressively reaches deeper layers, with a rate that depends on concrete properties (mainly its "permeability") and exposure conditions (mainly the humidity content in the concrete) [1]. When the carbonation front reaches the depth of the reinforcement, the steel is in contact with an almost neutral material and corrosion initiates. After initiation, steel corrosion will propagate with a rate that depends on the humidity content in the concrete [2]. In carbonated concrete, the corrosion rate is negligible (i.e. lower than 1 mA m^{-2}, which means roughly 1 μm $year^{-1}$) in dry conditions, but can reach values higher than 10 mA m^{-2} in wet conditions. Consequences of steel corrosion in concrete are the well-known processes of cracking, delamination and spalling of concrete cover, and this corresponds to the reaching of design limit states that define the end of the service life for the structure [3, 4]. This will occur in a period of time, called propagation time, which depends on corrosion rate. Considering for instance a threshold value of corrosion penetration of 100 μm to produce concrete cracking, the propagation time will be about 10 years for corrosion rates of 10 mA m^{-2} and 100 years for corrosion rates of 1 mA m^{-2}. Sometimes the end of the service life may even be defined by the presence of stains of corrosion products on the concrete surface, which cannot be accepted in the case of structures of architectural or aesthetic value or buildings and monuments that belong to the cultural heritage due to their historical relevance.

Once carbonation-induced corrosion of the reinforcement has initiated, it can be stopped in two ways: either by keeping the concrete dry (so that corrosion will not

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propagate because of the lack of humidity) or by restoring steel passivity (so that corrosion will be hindered by the protective passive layer) [4–7]. Hydrophobic treatments can be used to prevent water absorption in the concrete (e.g. when concrete is in contact with the rain) and so to maintain its humidity below a critical level; these treatments need to be re-applied rather often in time because of their scarce durability. Repassivation of steel can be obtained by replacing the carbonated concrete with a new alkaline material. The replacement of concrete is usually indicated as "conventional repair" [4] and consists in the removal of all the concrete that is carbonated at the depth of the rebars and that cannot guarantee protection from corrosion until the end of the desired residual service life and its substitution with a new alkaline material, usually a mortar. If this intervention is carried out according to specifications [5–8] and if an adequate layer of concrete or repair mortar covers the reinforcement, this method can guarantee that the structure will be protected from the consequences of corrosion until the end of its service life. However, this type of repair may require to remove large amounts of carbonated, although mechanically sound, concrete [9]. This may be undesirable, for instance, for conservation reasons (if it is required to preserve the original materials and surfaces [10]), for practical reasons (if it is not possible to generate noise, dust and debris), for geometric reasons (if it is not possible to give an adequate cover to the rebars) or, finally, for economical reasons (replacement of large amounts of mechanically sound concrete). For any of these reasons, the conventional repair is often strongly hindered by those who administrate the structures.

The application of electrochemical techniques is also possible to repassivate the steel in carbonated concrete and to stop carbonation-induced damage [11]. Compared to the conventional repair, electrochemical techniques can promote the repassivation of the reinforcement without removing the concrete, provided it is not damaged, by means of the application of a cathodic current, either permanent (as with cathodic protection, CP) or temporary (as with electrochemical realkalisation treatment, ER) [4].

Electrochemical realkalisation is based on the application of currents of 1–2 A m^{-2} with respect to steel surface [4, 12–14]. During the treatment, hydroxyl ions are produced at the rebar surface and, at the same time, carbonate ions penetrate from the surface of the concrete through electro-osmosis, diffusion and/or capillary absorption (there is still some debate on the main mechanism involved, see for instance [15, 16]). As the treatment proceeds, the alkaline regions may extend to the whole thickness of the concrete cover.

Electrochemical realkalisation has been introduced at the end of the 1980s [17, 18]. Hundreds of thousands of square metres have been treated, mainly in Northern Europe and North America [12, 13, 19–24]. Several laboratory experimental works proved that the application of a current of 1–2 A m^{-2} for few weeks can induce the complete realkalisation of concrete covers of 20–30 mm [15, 25–27]. However, few data are available on the effects of the composition of concrete on its realkalisation and also on the durability of the treatment [28]. Moreover, the effectiveness of the treatment in repassivating the steel, and so in stopping its corrosion, has been questioned [29, 30].

An experimental research was carried out with the aim of investigating some aspects connected with the application of ER and CP to carbonated concrete, considering the effects of the composition of concrete (in terms of cement type, water/cement (*w*/*c*) ratio and chloride content), the exposure conditions (wet environment or dry environment) and the presence of considerable amounts of corrosion products on the steel surface before the application of the techniques (i.e. pre-corrosion of the steel bars in the concrete). This article presents and discusses the results of ER tests; the results of *CP* tests will be dealt with in Part II [31].

2 Experimental

Reinforced concrete specimens were subjected to accelerated carbonation and then to ER tests.

2.1 Materials, specimens and exposure conditions

Cylindrical reinforced concrete specimens were cast, with the geometry shown in Fig. 1. Each specimen consisted of a concrete cylinder (diameter 60 mm) containing a ribbed carbon steel bar (diameter 10 mm) along its axis. The rebars were pickled in an inhibited acid solution, cleaned with a metal brush and stored in a desiccator until casting of the specimens. An activated titanium electrode (mixed

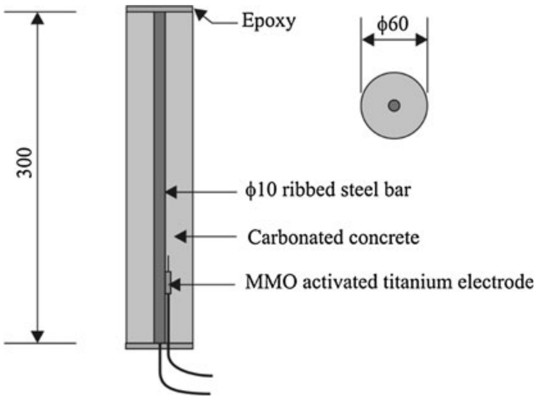


Fig. 1 Geometry of the specimens (mm)

metal oxide, MMO) for potential measurement was fixed to the rebar in the lower part of the specimen.

Six different concrete mixes were considered: their composition is shown in Table 1. Four concrete mixes (*A*, *B*, *C* and *D*) were made with limestone Portland cement (CEM II/A-LL 42.5R according to EN 197-1 [32]) with *w*/*c* ratio of 0.55 and 0.70 and with or without the addition of chloride (0.4% by mass of cement, added as calcium chloride to the water mix). The other two concrete mixes (*E* and *F*) were made with ground granulated blastfurnace slag cement (CEM III/B), with *w*/*c* ratio equal to 0.55 and 0.70. The relatively high values of *w*/*c* ratios chosen for the concrete mixes stemmed not only from the need to reduce the time necessary for subsequent carbonation, but also from the fact that such values are not unrealistic for real structures built in the past. A commercial acrylic superplasticiser was added to all mixes so as to obtain a consistence class *S4* (slump > 160 mm according to EN 206-1 [33]). Also cubic specimens (with side of 100 mm) were cast to be used for measurements of compressive strength, carbonation depth and total soluble chloride analysis (the measured chloride content referred to concrete mass is reported in Table 1).

Specimens were demoulded the day after casting and cured at 95% RH and 20 °C for a week. Then, four cubes for each type of concrete were kept in the curing chamber for 28-day and 90-day compressive tests, whilst the cylindrical specimens were provided with electrical connections to the steel bar and to the MMO electrode and isolated with epoxy on both bases, and then, together with sacrificial cubic specimens, were subjected to accelerated carbonation by exposure to a chamber with 60% RH and with a continuous flux of carbon dioxide.

The carbonation depth of each type of concrete was measured on the sacrificial cubes, by means of phenolphthalein test. Phenolphthalein is a pH indicator that has a dark pink colour in contact with environments with pH higher than 9, whilst it remains colourless for lower values of pH, and so it is suitable to distinguish between alkaline concrete and carbonated concrete [4]. When a carbonation depth of at least 25 mm (i.e. equal to the concrete cover of the cylindrical specimens) was reached on the cubes, the actual carbonation of each cylindrical specimen was verified on a thin slice (5–10 mm) cut perpendicularly to its axis.

Two different exposure conditions were considered: one at 98% RH (obtained in a chamber in equilibrium with liquid water) and the other at 85% RH (obtained in a chamber in equilibrium with a saturated potassium chloride solution). For the sake of simplicity, these conditions will be indicated as “wet environment” and “dry environment”, respectively.

The specimens were aged for about 1 year after the end of the carbonation period. During the ageing period, some specimens were exposed to the wet environment to promote the corrosion of the steel bar (*pre-corroded* specimens). The ER treatment begun after a further period of about 3 months of conditioning either in wet or dry environment. The ER treatment was also applied to some young specimens, i.e. immediately after the carbonation period. All the tests were carried out at room temperature.

Table 1 Composition and main properties at fresh and hardened state of the concrete mixes

Designation of mix	*A*	*B*	*C*	*D*	*E*	*F*
w/*c*	0.55	0.55	0.70	0.70	0.55	0.70
Cement type	CEM II/A-LL 42.5R				CEM III/B 42.5R	
Added chlorides (mass% cement)	–	0.4	–	0.4	–	–
Mix proportions						
Cement (kg m^{-3})	360	360	285	285	365	285
Water (kg m^{-3})	200	200	200	200	200	200
Crushed limestone aggregates with maximum size of 12 mm (kg m^{-3})	1800	1800	1872	1872	1800	1872
Calcium chloride $CaCl_2 \cdot 2H_2O$ (kg m^{-3})	–	2.99	–	2.36	–	–
Acrylic-type superplasticiser (kg m^{-3})	3.2	3.2	2.8	2.6	3.4	2.4
Measured properties						
Slump (mm)	230	200	240	230	190	205
28-day strength (MPa)	54.5	52.9	39.9	43.2	44.8	37.1
90-day strength (MPa)	55.6	63.1	47.0	46.5	49.0	41.1
Measured chlorides (mass% concrete)	0.01	0.06	0.01	0.05	0.03	0.03

2.2 Realkalisation tests

The ER treatment consisted in the application of a cathodic current density of 1 A m^{-2} for 3 weeks (total charge of 500 A h m^{-2} referred to steel surface). The current was supplied by an activated titanium mesh anode placed around the surface of the specimen. The electrolyte was cellulose pulp soaked with an alkaline solution of sodium carbonate (1 M). Each specimen was connected to a DC current feeder: the steel bar to the negative pole and the MMO-activated titanium mesh to the positive pole. During the treatment, the current was constantly monitored, as well as the potential of the steel versus the internal MMO electrode with on–off technique (instant-off potential was measured within 1 s). The internal MMO electrode was periodically calibrated versus an external SCE electrode placed on the lateral surface of the specimen, in the vicinity of the internal electrode.

The realkalisation of concrete was periodically measured by cutting a slice of the specimen perpendicular to its axis, approximately 30-mm thick, and spraying the freshly cut surface with phenolphthalein solution. The measurements of realkalised thickness on the cut section were carried out in four points, along four perpendicular directions, and then the average internal and external values were calculated. The average external values were expressed in terms of the distance from the surface of the rebar (for instance, an external thickness of 3 mm was expressed as (25 − 3) mm = 22 mm). When the internal and external fronts overlapped, it was not possible to distinguish between the two fronts, and both layers were set arbitrarily equal to half of the concrete cover (12.5 mm).

After the treatment, the specimens were exposed to the same conditioning environment as before the treatment (wet or dry). The corrosion conditions of the rebars were monitored by means of potential and polarisation resistance measurements. The polarisation resistance measurements were carried out with a potentiostat by applying a potential difference of ±10 mV with respect to the free corrosion potential, by means of an external counter electrode, and measuring the circulating current after 30 s from the potential variation; the polarisation resistance R_p was obtained as the average of the two slopes $R_p = \text{avg}(\Delta E/I)$ and the corrosion rate was evaluated as $V_{corr} = \text{cost}/(R_p S)$ with cost = 26 mV and S = surface of the steel bar [34, 35].

After 9 months of exposure to the conditioning environment, the specimens were subjected to potentiostatic anodic polarisation tests to investigate on the repassivation of steel in contact with the realkalised concrete. The steel bar was polarised at +100 mV/SCE for 24 h by means of an external counter electrode of activated titanium, and the current was monitored. For comparison purpose, the tests were carried out also on carbonated specimens not subjected to the ER treatment (in this case, the duration of the anodic polarisation tests was lower, 5–6 h, due to the high currents measured). At the end of the tests, the specimens were split axially to observe the corrosion conditions of the rebars and repeat the phenolphthalein test along the whole length of the specimens.

3 Effects of the realkalisation treatment

The ER tests were aimed both at studying the realkalisation of concrete during the treatment and at investigating the corrosion conditions of the rebars afterwards. The aim of the ER treatment is to recreate an alkaline environment around the rebar so as to promote conditions favourable to steel repassivation; it is therefore essential to know the factors that influence the realkalisation of concrete.

3.1 Realkalisation of concrete

The phenolphthalein tests carried out during the treatment allowed to follow the progress of the realkalisation of concrete on each specimen. The evolution of realkalisation in the concrete cover was monitored during the application of the current. For instance, Fig. 2 shows results obtained after 3, 7, 14 and 21 days of treatment at 1 A m^{-2} on one of the specimens made with CEM III/B and *w/c* ratio of 0.55 (concrete *E*) [22]. Realkalisation occurred in two directions: from the rebar towards the surface of the specimen (internal front), due to the production of alkalinity induced by the applied cathodic current, and from the surface of the specimen towards the rebar (external front), due to the penetration of the alkaline solution in contact with the anodic system. At the end of the treatment, after 21 days, the internal and external fronts overlapped along the most of the circumference. Figures 3, 4 and 5 show the position of the inner and outer realkalisation fronts as a function of the time of treatment; these results were obtained on young specimens, i.e. immediately after the carbonation period, and were confirmed later on specimens aged for a year. The axial symmetric geometry of the cylindrical specimens implies that the inner and outer thicknesses are not equivalent. However, some useful considerations can be made by comparing the values obtained with different types of concrete on specimens with the same geometry.

It can be seen that all the specimens made with concrete with *w/c* ratio of 0.70 (*C*, *D* and *F*) showed thicker alkaline layers, from both fronts, compared to specimens made with concrete with *w/c* ratio of 0.55 (*A*, *B* and *E*). The former were realkalised almost completely at the end of the treatment: as a matter of fact, both internal and external

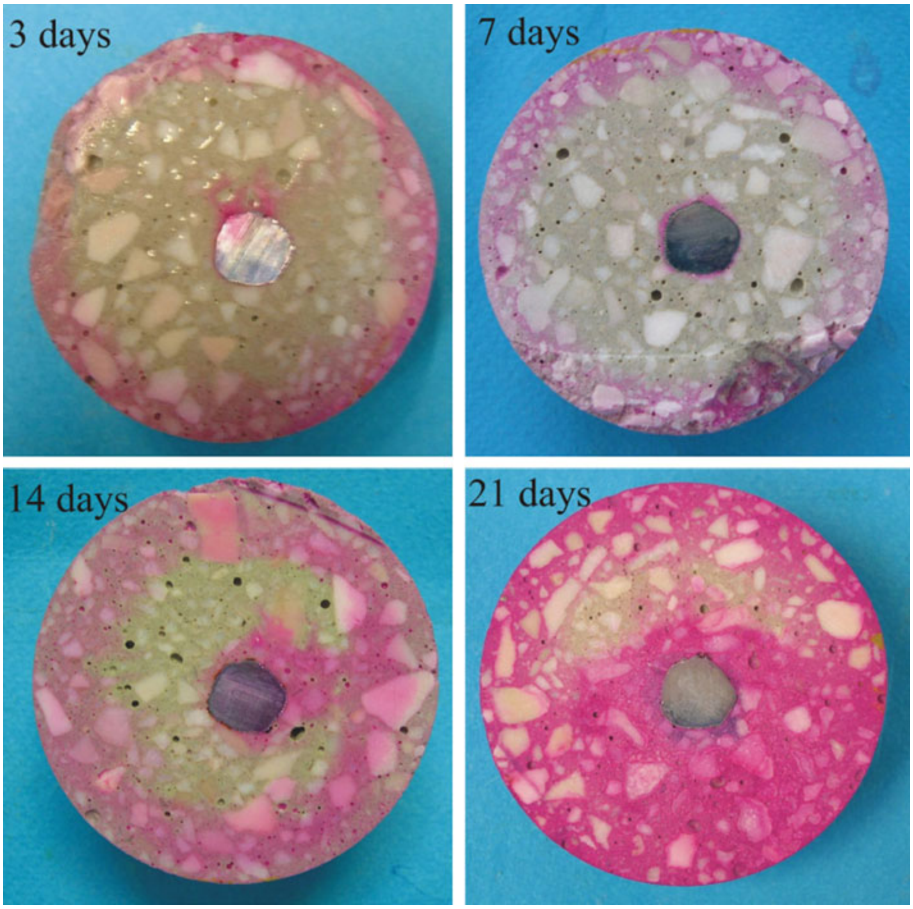


Fig. 2 Evolution of realkalisation fronts detected with phenolphthalein test during the application of 1 A m^{-2} on the rebar of a young specimen made with CEM III/B and *w*/*c* 0.55 (concrete *E*) [22]

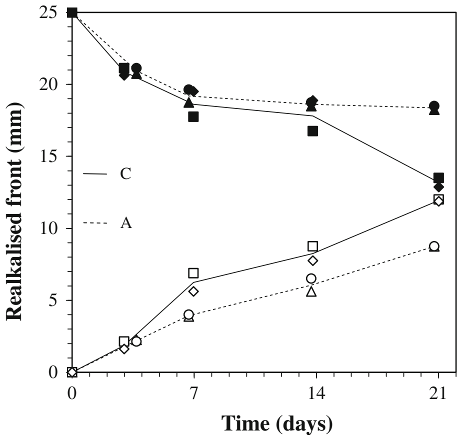


Fig. 3 Position of internal (*white*) and external (*black*) realkalisation fronts in the concrete cover as a function of time for specimens made with concrete with CEM II/A-LL and *w*/*c* of 0.55 (*A*, symbols *triangle* and *circle*) and concrete with CEM II/A-LL and *w*/*c* of 0.7 (*C*, symbols *square* and *diamond*) [22]

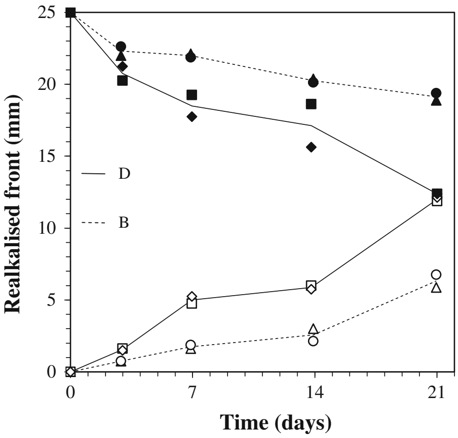


Fig. 4 Position of internal (*white*) and external (*black*) realkalisation fronts in the concrete cover as a function of time for specimens made with concrete with CEM II/A-LL, *w*/*c* of 0.55 and 0.4% chlorides (*B*, symbols *triangle* and *circle*) and concrete with CEM II/A-LL, *w*/*c* of 0.7 and 0.4% chlorides (*D*, symbols *square* and *diamond*) [22]

thicknesses were close to 12.5 mm (i.e. half the nominal thickness of the concrete cover), indicating that the internal and the external layers of realkalisation overlapped. The specimens made with a *w*/*c* ratio of 0.55, on the other hand, showed lower realkalised layers both from the rebar and from the external surface, and, at the end of the treatment, the specimens showed an area of still carbonated concrete. A difference in the *w*/*c* ratio implies a difference in the porosity of the cement paste. The higher porosity of the

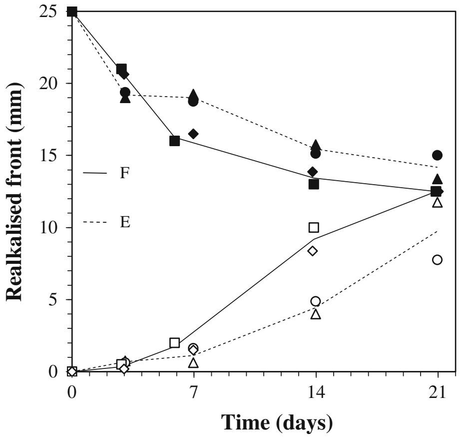


Fig. 5 Position of internal (*white*) and external (*black*) realkalisation fronts in the concrete cover as a function of time for specimens made with concrete with CEM III/B and *w*/*c* of 0.55 (*E*, symbols *triangle* and *circle*) and concrete with CEM III/B and *w*/*c* of 0.7 (*F*, symbols *square* and *diamond*) [22]

cement paste with *w*/*c* of 0.70 enhanced the spread of alkalinity, the one produced by the cathodic reaction and the one due to the penetration of the alkaline electrolyte, and allowed to extend the effects of the treatment to larger areas. These results are in agreement with those obtained by Mietz [15].

Also the types of cement showed an influence on realkalisation: for concrete mixes made with ground granulated blastfurnace slag cement, higher values of realkalised thicknesses were obtained, in particular, from the external surface: the position of the external front was 15 mm (which corresponds to an external layer of realkalisation of 10 mm) even for the *w*/*c* ratio of 0.55, whilst in specimens made with limestone cement it was 18–20 mm (i.e. the external layer of realkalisation was 5–7 mm). However, the internal realkalisation in specimens with slag cement at short times of treatment (3 and 7 days) was considerably lower than in the other specimens. This could be related to the lower alkalinity and lower porosity of concrete made with slag cement compared to limestone cement.

In specimens with mixed-in chlorides, the development of the internal alkaline front was slower compared to that in specimens without chlorides (compare Fig. 3 with Fig. 4). This result can be due to the contribution of chlorides to the transport of current, which is beneficial in moving chloride ions away from the concrete in contact with the steel, reducing the local aggressiveness, but reduces the amount of hydroxyl ions that contribute to the current, and so the spread of alkalinity. So, in the presence of chlorides, even in small amounts, a higher amount of circulated charge is necessary to obtain a certain layer of realkalisation, compared to chloride-free concrete, and therefore, at a given current density, the treatment should last for longer periods to realkalise the whole cover thickness. To this regard, it should be noted that the specimens made with ground granulated blastfurnace slag cement (*E* and *F*) contained 0.03% of chlorides by mass of concrete (Table 1), coming from the slag that was probably quenched with sea water, and this may have contributed to the reduction of the internal development of alkalinity at short times.

These results show that an accurate design of the treatment of realkalisation requires a preliminary investigation on concrete composition and an accurate control of the effects of the treatment. The criteria commonly used in practice (for instance, a total circulated charge of 200 A h m^{-2} [14]) are only approximate indications, as for a given applied current density and period of treatment the actual realkalisation depends on the characteristics of the material, as well as on geometrical factors, such as the thickness of the concrete cover. The amount of realkalisation itself, simply evaluated by measuring the layer of alkaline concrete with phenolphthalein test, as it is commonly done in practice, gives an important indication on the progress of the treatment, but cannot be considered as an absolute criterion, since a higher thickness can simply result from a high porosity, and so does not necessarily indicate a more durable realkalisation. It should be noted that literature data on the effect of cement paste porosity on the rate of re-carbonation after the treatment are totally lacking, both from laboratory tests and from field applications.

After the ER treatment, the specimens were exposed to a dry or a wet environment, and the corrosion conditions of steel were monitored (see Sect. 3.2). It should be noted that, although some of the specimens had not been realkalised over the entire concrete cover, they were all alkaline for at least 7–8 mm around the rebars, as it can be seen in Figs. 3, 4 and 5 and as it was also confirmed from the statistical analysis of values of potential of the MMO electrodes placed inside the specimens, that is reported in Fig. 6 (the analysis was done including all the specimens since no effect of concrete composition was evident). The potential of MMO internal electrodes depends on the pH of the concrete pore solution, and so these electrodes can be used to detect concrete realkalisation in a non-destructive way [36, 37]. Before the application of the treatment, the distribution of the potential measured versus an external SCE reference was characterised by values between 100 and 200 mV/SCE, whilst after the treatment a separate distribution was obtained that was shifted towards more negative values, between −200 and 0 mV/SCE, which are typical of alkaline concrete. This is a further proof that in each specimen subjected to ER treatment the steel bar was in contact with an alkaline concrete along its entire length.

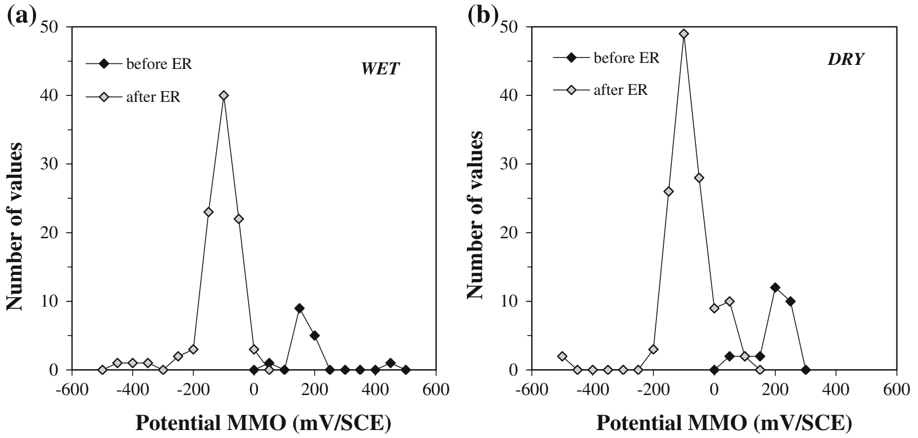


Fig. 6 Distribution of frequency of potential of internal MMO electrodes measured in all the specimens before and after the ER treatment, in the wet (**a**) and dry (**b**) environment

3.2 Corrosion conditions of steel

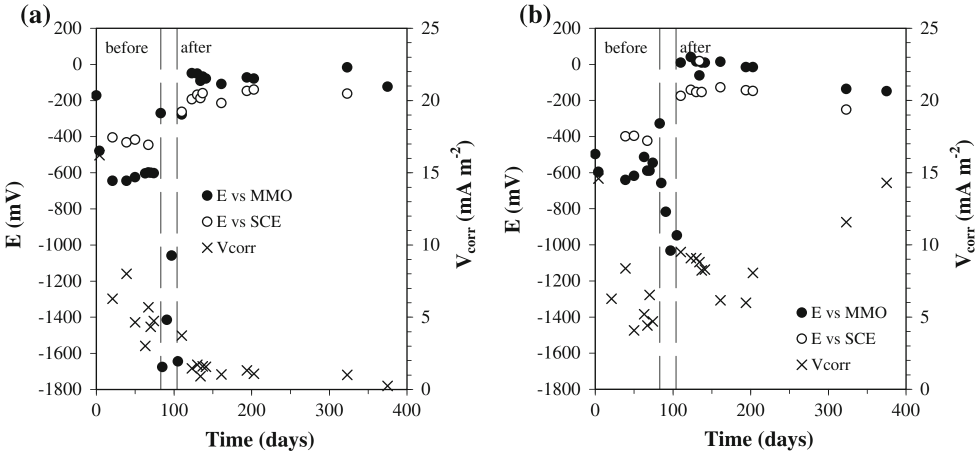
The corrosion conditions of steel reinforcement were investigated by means of electrochemical measurements of free corrosion potential and corrosion rate. In order to investigate on the repassivation of steel, the values of steel potential and corrosion rate measured after the treatment were compared with those measured before the treatment on the same specimen. For instance, Fig. 7a shows the results obtained on a specimen made with CEM II/A-LL and *w/c* of 0.55 (concrete *A*) exposed to the dry environment before and after the treatment (steel potential is plotted both versus the MMO internal electrode and versus the external SCE electrode). It can be seen that before ER the steel was characterised by potential values around −400 mV/SCE (corresponding to −650 mV/MMO) and an average corrosion rate of about 6 mA m^{-2}. During the treatment the instant-off potential of steel reached values as low as −1.7 mV/MMO, due to the strong cathodic polarisation (during the treatment, steel potential was measured only versus MMO internal electrode). After the treatment, the steel potential increased to values around −200 mV/SCE or higher, and corrosion rate decreased to values with an average around 1 mA m^{-2}, which can be considered negligible. This example represents the expected situation of effectiveness of the treatment, and it suggests that the steel has undergone repassivation, as indicated by the increase in potential values of steel and decrease of corrosion rate to negligible values.

However, this was not the case for all the specimens: for instance, Fig. 7b shows the results that were obtained on a specimen made with CEM II/A-LL and *w/c* of 0.70 (concrete *C*) and with *pre-corroded* steel bar: steel potential passed from −400 to −200 mV/SCE, as for specimen *A*, however corrosion rate increased, and even values higher than 10 mA m^{-2} were measured after the treatment.

Figure 8 summarises the results of average corrosion rate before and after the treatment in wet and dry environment, in the different concrete mixes considered. Before the treatment, i.e. in carbonated concrete, the corrosion rate of steel was between 10 and 20 mA m^{-2} in the wet environment, whilst in the dry environment a great scatter of corrosion rate values was obtained, with values as low as 6 mA m^{-2} up to values of 90 mA m^{-2}. In the dry environment, where all the concrete mixes were available, the corrosion rate increased both in the presence of chlorides, even in small amounts, and in the presence of a higher porosity due to a higher *w/c* ratio. For instance, in chloride-free concrete with CEM II/A-LL and *w/c* of 0.55, the corrosion rate was about 6 mA m^{-2}; this value increased to 12 mA m^{-2} for a *w/c* of 0.70 and to 20 mA m^{-2} for a chloride content of 0.4%. Corrosion rate values in specimens with CEM III/B were similar to those with CEM II/A-LL and the same *w/c*.

Considering the corrosion conditions of steel after the ER treatment, in the wet environment (Fig. 8a), the corrosion rate of steel clearly decreased for non *pre-corroded* specimens: however, these values were still relatively high, i.e. close to or even higher than 5 mA m^{-2}. In the case of *pre-corroded* specimens (indicated with *C** and *D** in the figure), the corrosion rate was even higher after the treatment than before. Also in the dry environment (Fig. 8b), a clear decrease of the corrosion rate in the non *pre-corroded* specimens was measured: on concrete mixes *A*, *B*, *C* and *E*, the average values were negligible, whilst for concrete *D* it was around 5 mA m^{-2} and for concrete *F* it was still higher than 15 mA m^{-2}. Also in dry conditions, the *pre-corroded* specimens had apparently no benefits from the treatment, with similar values of corrosion rate (as for specimen *D*) or even higher values (as for specimens *C* and *F*) compared to those before the treatment. It was also noted that some of the *pre-corroded* specimens showed cracking of concrete cover, in particular, this occurred on specimen *F* in the dry environment and on specimens *C* and *D* in the wet environment.

Fig. 7 Potential of steel bar measured versus internal MMO and external SCE reference electrodes and corrosion rate before and after the ER treatment in a specimen made with CEM II/A-LL and *w*/*c* of 0.55 (concrete *A*, **a**) and in a specimen made with CEM II/A-LL, *w*/*c* of 0.70 and *pre-corroded* reinforcement (concrete *C*, **b**), both in the dry environment



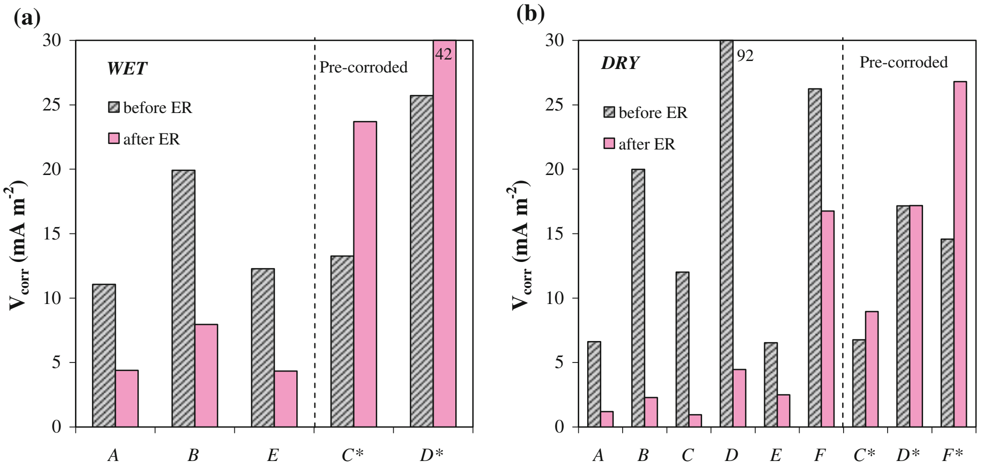


Fig. 8 Average values of corrosion rate of steel bars measured before and after the ER treatment, in the wet (**a**) and dry (**b**) environment, for different concrete mixes

Although the measurements of corrosion rate with polarisation resistance after the application of ER should be carefully interpreted and are still debated [38, 39], the results reported in Fig. 8 indicate a clear trend that should be clarified to assess the complete reliability in the application of the realkalisation treatment that, being a repair technique, is likely to be applied on already corroded steel reinforcement. It should be reminded that the ER technique has been applied for years and no cases of failure have ever been reported [12, 13]; however, some authors have questioned its effectiveness on the basis of laboratory tests, in particular, in the presence of considerable amounts of corrosion products [29, 30] and an increase in the corrosion rate of steel after the treatment has been reported [40]. It is hard to explain why a cathodic current should promote steel corrosion in concrete; it seems more likely that the linear polarisation technique may not be suitable to measure corrosion rate after the treatment. The cracking of some specimens, however, suggests that corrosion actually propagates even after the treatment. This aspect should be clarified to establish reliable monitoring methods to check the treatment effectiveness.

Figure 9 reports the steel potential as a function of the corrosion rate: in spite of the high scatter typical of these measurements, it is clear that the values of steel potential and corrosion rate after the treatment, although they are respectively higher and lower than those before the treatment, are not those expected in case of repassivation, i.e. corrosion rate lower than 1 mA m^{-2} and potential higher than 0 mV/SCE that characterise passive steel in alkaline concrete. Moreover, data from the *pre-corroded* specimens (white symbols) lay outside the correlation, showing high values of corrosion rate and high values of potential after the treatment. Also the steel potential values were statistically analysed: it was preliminary checked that concrete composition had a negligible effect on steel potential and so, in the distributions reported in Fig. 10, all the specimens were considered together. It can be seen that both in wet and dry environment and both for non *pre-corroded* and *pre-corroded* specimens an increase in steel potential was observed after the treatment from −400/−500 to −200/−250 mV/SCE.

So there is a discrepancy between results from potential measurements, that are consistent with repassivation of steel, and results from polarisation resistance measurements, that indicate active corrosion of steel. In order to further investigate this subject, potentiostatic anodic polarisation tests were carried out after about 9 months from the end of the treatment (except on cracked specimens). The tests were carried out also on reference carbonated specimens not subjected to the ER treatment. Figure 11 compares the current densities measured after 3 h of application of a potential of +100 mV/SCE to steel. This potential value was chosen since it represents the upper limit for passive steel in concrete exposed to the atmosphere and at this potential values, 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 [15]. In carbonated concrete, the current density was very high, several thousands of mA m^{-2}, whilst in the realkalised specimens, it was 10–100 mA m^{-2}, considerably lower than those in carbonated concrete, but still much higher than those usually measured on passive steel in alkaline concrete, which are of the order of 1 mA m^{-2} or even lower.

Following the potentiostatic tests, the specimens were broken to observe the corrosion conditions of steel and repeat phenolphthalein test. The specimens were broken axially to observe the rebars along their entire length. Most of the steel bars turned out to be free from significant amounts of corrosion products; when corrosion products were present, they were localised in the lower part of the specimen, close to the internal MMO electrode. Indeed, whilst most of the concrete in contact with the steel bar was still alkaline, local carbonated zones were detected in the lower part of the specimens. This could be due to an uneven distribution of current, although care had been taken to this regard during the treatment (a shielding effect of the MMO electrode can be hypothesised). In particular the specimens that had undergone cracking showed the presence of still carbonated concrete at their base. Therefore, it is reasonable that the propagation of corrosion that occurred in some of the specimens was due to the presence of steel areas in contact with carbonated concrete that could actively corrode and gave high contributions of exchanged current in linear polarisation tests and in potentiostatic polarisation tests.

Although it indicates the effectiveness of the treatment in stopping steel corrosion, the lack of significant amounts of corrosion products on the surface of the steel bar that was observed after 9 months of exposure to the wet environment is not consistent with the high values of measured corrosion rate. This confirms that the monitoring of the effectiveness of ER cannot be carried out with techniques that involve the measurement of the current. However, further investigations are needed to clarify this aspect, in particular, in relation with the role of the pre-corrosion of the steel.

4 Conclusions

The thickness of realkalised concrete, evaluated with phenolphthalein test, was higher for specimens made with a *w/c* ratio of 0.70 compared to specimens with a *w/c* of 0.55, both for the contribution due to the cathodic reaction at the steel surface (internal) and for the contribution due to the ingress of the alkaline solution (external). Also the presence of chlorides in the concrete influenced the amount of realkalisation, reducing the internal layer. Specimens made with ground granulated blastfurnace slag cement, compared to limestone portland cement, showed thicker realkalised external layers, but lower realkalised internal layers, in particular after short times of treatment.

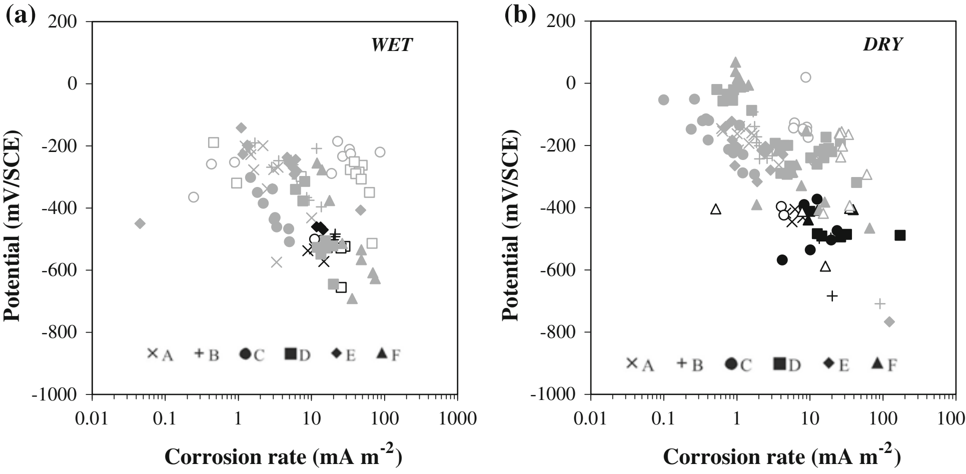


Fig. 9 Values of corrosion potential as a function of corrosion rate of steel bars measured on all the specimens before (*black symbols*) and after (*grey symbols*) the ER treatment, in the wet (**a**) and dry (**b**) environment. *Pre-corroded* specimens are indicated with *white symbols*

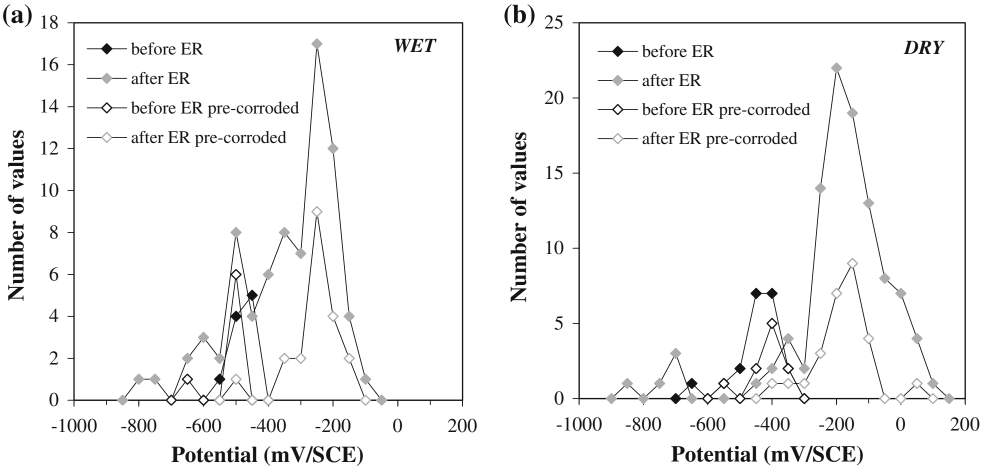


Fig. 10 Distribution of frequency of free corrosion potential of steel bars measured in all the specimens before and after the ER treatment, in wet (**a**) and dry (**b**) environment

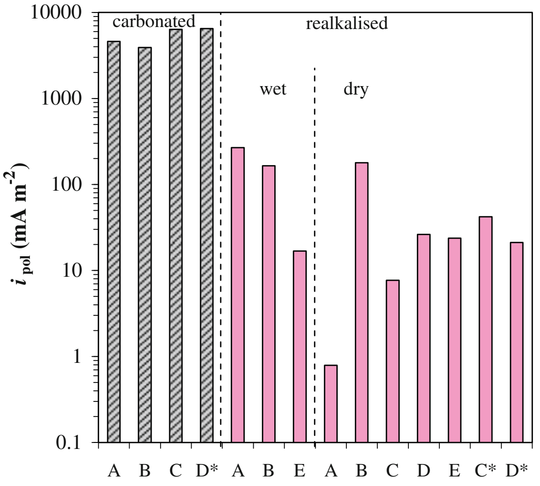


Fig. 11 Current density measured after 3 h of potentiostatic polarisation at +100 mV/SCE on reference carbonated specimens and on specimens subjected to ER treatment (*Asterisk* indicates *pre-corroded* specimens)

The corrosion conditions of steel were monitored with electrochemical measurements of free corrosion potential and corrosion rate. Steel potential values after the treatment were higher than before the treatment, as it is expected after repassivation takes place. Steel corrosion rate measured by polarisation resistance showed a clear reduction after the treatment, both in the wet and dry environment; however, values around 5 mA m^{-2} or higher were obtained, in particular, for specimens in the wet environment and containing chlorides. These values are much higher than those expected for passive steel in alkaline concrete. The specimens whose reinforcement had undergone considerable corrosion before the application of the ER treatment (*pre-corroded*) even showed an increase in the corrosion rate after the treatment, both in wet and dry conditions. The current circulating in the realkalised specimens during potentiostatic polarisation test was considerably lower than that in carbonated concrete, but still much higher than that typical of passive steel in alkaline concrete.

The direct observation of steel after destruction of the specimens highlighted that the small amount of corrosion products was not consistent with the high values of corrosion rate measured with the linear polarisation technique. The results obtained with electrochemical measurements indicate some evidence of steel repassivation, but cannot ascertain it, in particular, for *pre-corroded* specimens. Further studies are needed to clarify aspects connected with the monitoring of corrosion conditions of steel after the ER treatment.

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