Macroscopic observations on the long-term effects of cathodic protection applied to carbonated reinforced concrete

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Abstract
The aim of the paper was to study macroscopic long-term modifications induced by cathodic protection applied to carbonated concrete, in order to localise possible deterioration phenomena that can affect the performance of the protection system. Carbonated reinforced specimens that had been subjected to cathodic protection for 13 years were analysed with phenolphthalein indicator, that allowed to highlight a pH reduction in the originally alkaline mortar in which the anode was embedded. The pH reduction was localised in the mortar in contact with carbonated concrete, rather than directly in contact with the anode. The thickness of the layer with reduced pH increased with the circulated charge and was nil on specimens that were not subjected to current application. This modification was attributed to a mechanism of dissolution of calcium hydroxide in the mortar. Although a thorough qualitative and quantitative description of the modifications requires further investigations, the results provide a better understanding of possible deterioration phenomena at the anode and they indicate that such phenomena may be hindered by embedding the anode mesh in an adequate layer of alkaline mortar and keeping the current at the least value that is necessary to protect the steel from corrosion.

Keywords
Anode, carbonation, cathodic protection, corrosion, pH indicator, reinforced concrete.

Introduction
The durability of reinforced concrete structures may be limited by corrosion of steel reinforcement, and it is one of the big challenges of the new century, both for new and existing structures [1,2]. While for new structures accurate procedures of design and construction, possibly combined with the resort to smart, sustainable and innovative materials, can allow to guarantee long service lives even in aggressive environments, for existing structures the primary need to restore safety and serviceability for a long enough residual service life is often accompanied by the requirement to preserve as much as possible the original materials, in order to limit the impact of the intervention on the structure and the environment [3-5]. To this regard, cathodic protection is one of the repair techniques that can allow a good compromise between these often opposing requirements [6,7].

   Cathodic protection (CP) is an electrochemical method based on the application of a permanent cathodic current to steel reinforcement, as it is depicted in Figure 1 [8-10]. CP is traditionally applied as a repair method in aggressive environments characterised by the presence of chlorides, as marine environments or exposure to de-icing salts; more recently, it was proposed as a repair method also for concrete suffering carbonation-induced corrosion, due to its advantages connected with the possibility of leaving non-protective (i.e. carbonated) but mechanically sound concrete in place, hence avoiding the removal operations that often imply the generation of noise, dust and large amounts of waste [11-13].

Whilst the effectiveness of CP in protecting steel reinforcement from corrosion has been widely investigated, and CP is considered the only technique that can control corrosion of steel in contact with a non-protective concrete, the effects of the circulating current on the overall cathodic protection system, including concrete and anode system, have received less attention in the scientific literature [14-16]. In fact, besides providing protection to steel from corrosion, CP promotes other modifications related to transport phenomena induced by the applied current (Figure 1), that may affect the durability of the CP system as a whole.

In particular, the production of acidity due to the electrochemical reactions at the anode has often been considered one of the main factors affecting the durability of the CP system, since it may interact with alkaline components of the cementitious material in which the anode is embedded [17-19]. For instance, inert anodes made of an activated titanium mesh embedded in mortar and applied on the concrete surface are considered the most durable since they have service lives of the order of 50 or even 100 years, provided the applied current does not exceed a threshold value of the order of 100 mA m^{-2} referred to the anode mesh [20,21]. However, this indication is mainly of empirical nature and a thorough description of the deterioration phenomena that may occur is not available yet.

This paper presents and discusses the results obtained on carbonated concrete specimens subjected to CP for 13 years. The original aim of the research was to study the effectiveness of CP in protecting steel from corrosion and it was discussed elsewhere [11,12]. After interruption of the tests, the specimens were used to characterise the macroscopic modifications produced on the long term by the applied current, both on concrete and on the anode system, in relation with possible deterioration phenomena that may limit the service life of CP systems.

Materials and methods

Reinforced specimens made of initially carbonated concrete were subjected to CP tests. Each specimen had dimensions of 0.6 m × 0.2 m × 0.05 m and contained three steel bars with diameter of 10 mm (Figure 2). Concrete was mixed with 260 kg/m^3 of portland cement, 0.65 water to cement ratio and 2000 kg/m^3 of crushed limestone aggregate. The average compressive strength after 28 days of wet curing was 40 MPa. Some specimens were prepared with the same concrete mix with the addition of 0.4% chloride by weight of cement (added as calcium chloride in the mix water). Manganese dioxide reference electrodes were embedded near the central bar for monitoring of steel potential. Accelerated carbonation was performed in an environment with 5% CO_2 and 60% RH. After complete carbonation, an activated titanium mesh was applied on the largest surface, it was embedded in a layer of mortar and used as anodic system. All specimens were exposed to external unsheltered environment.

CP was applied to single specimens with current densities of 5 and 10 mA m^{-2} referred to steel surface; some of these specimens had previously been subjected to an initial current density of 70 mA m^{-2}. Double ("*sandwich*") specimens were obtained by joining two single specimens, so as to obtain two mats of rebars at different distance from the anode system; on these specimens, an average current density of 10 mA m^{-2} was applied. For specimens that were subjected to CP the activated titanium mesh of the anode was connected to the positive terminal of a current feeder, while the reinforcement was connected to the negative one (as it is shown in Figures 3a and 3b), and the current was switched on. Reference alkaline, carbonated and carbonated with chloride specimens were left in free corrosion conditions; the activated titanium mesh in the alkaline mortar was not used as anode but only for electrochemical measurements (Figure 3c). Table 1 summarises the tests performed on the various specimens and their duration.

The effectiveness of CP in protecting steel from corrosion was investigated by means of electrochemical measurements [11,12]. After about 13 years, the tests were interrupted and the specimens were used to characterise the effect of CP in terms of chemical modifications in the concrete and mortar. In this paper, macroscopic observations will be described. All specimens were cut perpendicularly to the steel bars, so as to obtain a section containing concrete, reinforcement,

anode system and their interfaces. The surface was washed and dried, and then sprayed with an alcoholic solution of phenolphthalein, which is a pH indicator that turns to pink for pH values higher than 9 and remains colourless for pH values lower than 9. This allowed to distinguish alkaline areas, which have a pH around or even higher than 13 (e.g. alkaline mortar or realkalised concrete), from areas with almost neutral pH (e.g. carbonated concrete). The thickness and extent of these areas were measured with a calliper.

Results

Figure 4 shows the section of an initially carbonated specimen subjected to CP at 10 mA m^{-2} after spraying the surface with the solution of pH indicator (in all pictures, the specimen is oriented with the anode system at the bottom). A realkalised area of concrete was detected around each steel bar, due to the realkalisation effect induced by the applied cathodic current. These areas had a circular, though irregular shape, their boundaries being not well defined, and they were visible even before spraying phenolphthalein, showing a lighter appearance compared to the surface of carbonated concrete. The rest of the concrete surface remained colourless after spraying phenolphthalein, as it is typical for carbonated concrete. No corrosion products of iron were visible at the steel/concrete interface.

The mortar of the anode system was mainly alkaline, except over a thin and roughly uniform layer in contact with carbonated concrete that showed a reduced pH; this layer was visible even before spraying with phenolphthalein, due to its lighter colour compared to the rest of the mortar, and had an average thickness of about 1.3 mm (Table 2). Conversely, no evidence of transport of alkalinity from the mortar towards the carbonated concrete was detected with phenolphthalein test.

Activated titanium wires of the anodic mesh, that were embedded in the alkaline region of the mortar, showed a good contact with the mortar itself. No area with reduced pH was detected on the surface of mortar exposed to the external environment, indicating no substantial penetration of carbonation in the mortar.

Similar findings were obtained on the specimen that also contained chlorides (Figure 5), except for the fact that the anode mesh, that was very close to the concrete surface and was embedded in the layer with reduced pH, was surrounded by voids with dimensions of several millimiters. Inside these voids white products as well as brown products (similar to rust) were visible. Also the specimens that were subjected to an initial current density of 70 mA m^{-2} showed similar pH distributions, in terms of realkalisation ring around steel bars and layer with reduced pH in the mortar close to carbonated concrete.

Figure 6 shows a specimen subjected to CP at 5 mA m^{-2}. The extent and colour intensity of realkalised concrete around steel were lower compared to specimens at 10 mA m^{-2}, however corrosion products were not detected at the steel/concrete interfaces. Areas with reduced pH were also present in the mortar of the anodic system adjacent to carbonated concrete, however they were not uniform and the average thickness was of 0.4-0.7 mm (Table 2). Moreover, next to areas of decreased pH in the mortar, also areas of spread of alkalinity from the mortar in the concrete were detected; these areas were mainly localised where the anode mortar was in contact with coarse aggregate, rather than with cement paste.

Figure 7 shows results of phenolphthalein tests on *sandwich* specimens. On the whole, the pH pattern was characterised by realkalisation of initially carbonated concrete around steel bars and alkalinity of the three portions of mortar (anode system, joining mortar and "anode system" of the second specimen, which indeed was not used to supply any current, as it was shown in Figure 3b). The realkalised area around steel was higher for the first mat, that was closer to the anode and received higher current, compared to the second mat, that was farther from the anode. In addition, the realkalised areas in the first mat extended towards the alkaline joining mortar and overlapped with it; nevertheless, the two regions were still distinguishable due to a different intensity of the colour (pink colouring was less intense for realkalised concrete compared to joining mortar). This occurred also on the second mat of rebars, whose realkalised concrete reached the top layer of

mortar. Layers with reduced pH were detected both in the anode mortar at the interface with carbonated concrete and in the joining mortar at the interface with carbonated concrete of the second specimen, although in the latter case the thickness was lower. Again, the wires of the anodic mesh were surrounded by macrovoids when they lay in the layer of mortar with reduced pH, both in the specimen with and without chlorides. Conversely, the titanium wires in the top layer of mortar (that were not used as anode, and so did not supply any current), were in contact with the embedding mortar. From this mortar, the alkalinity spread through the initially carbonated concrete, partially realkalising it.

Finally, on all the reference specimens – alkaline, carbonated and carbonated with chlorides (Figure 8) – the mortar of the anodic system was fully alkaline: areas with reduced pH were not detected either at the interface with concrete or at the surface exposed to the environment. The carbonated specimen showed the presence of alkaline regions of concrete on the surface in contact with the anodic system, while this was not the case for the specimen that also contained chlorides, where these regions were virtually absent. The activated titanium mesh (which was present also in reference specimens although it did not supply any current) was always completely in contact with embedding mortar.

Corrosion products were visible at the steel/concrete interfaces of the carbonated and carbonated with chloride specimens (Figures 8a and 8b). A crack was present on each specimen in correspondence to the central bar. This crack was detected on the external surface of the specimen before cutting and it was longitudinally running over the central bar; its propagation may have been favoured by cutting operations.

Finally, the alkaline specimen showed zones with reduced pH in concrete indicating penetration of carbonation from the surface exposed to the environment (Figure 8c). The average depth of penetration was around 10 mm. Nonetheless, the steel bars were still in contact with alkaline concrete and no corrosion products were detected around them.

Discussion

The high alkalinity of the hydrated cement paste in cementitious materials, such as concrete and mortar, is one of the main factors affecting the corrosion behaviour of embedded steel reinforcement. In addition, in a CP system the electrochemical reactions that occur at the surfaces of anode and reinforcement imply the production of acidity and alkalinity and are accompanied by transport phenomena induced by the current, as it was shown in Figure 1. Hence, detecting variations in pH is the first step in the understanding of possible modifications induced by the applied current.

The simple analysis of the cut section of each specimen with sprayed phenolphthalein, which is a pH indicator that clearly distinguishes alkaline regions (with pH higher than 9, usually around 13) from almost neutral regions (with pH lower than 9), allowed to highlight and localise some macroscopic modifications produced by the applied current.

The most evident feature that emerged from specimens subjected to CP was the presence of a layer with almost neutral pH in the mortar in contact with carbonated concrete, indicating that a local reduction of alkalinity occurred in the mortar at the interface with concrete, rather than in contact with the anode mesh where the source of acidity is located. This reduction was detected on all specimens subject to CP, whilst it was not detected on either reference specimens. Hence, it was likely related to the applied current. This modification had never been reported before at a macroscopic scale. However, it may be consistent with a mechanism of dissolution of calcium hydroxide that had been proposed to explain an observed increase of porosity at the interface between anode mortar and carbonated concrete under CP [17].

As a matter of fact, after about 6 years of tests, core samples were taken from the same slabs considered in this work; thin sections were prepared and analysed by means of polarisation and fluorescence microscopy (PFM) and wavelength dispersive electron microprobe [17]. These analyses highlighted the presence of a zone with increased porosity in the mortar in contact with the

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carbonated concrete (with thickness of about 0.5 mm), whilst only a slight increase of porosity was detected in the mortar in contact with the anodic mesh (with thickness of few μm). The increased porosity was accompanied by a reduction in the content of calcium and was attributed to a possible dissolution of calcium hydroxide crystals. The mechanism can be described as follows. In the alkaline mortar around the anode, sufficient hydroxyl ions (coming from sodium, potassium and calcium hydroxides) are available to neutralise acid formation at the surface of activated titanium mesh. At the mortar/concrete interface the situation is different: the pH in the carbonated concrete is low, so the pore solution contains hardly any hydroxide [22]. At the interface between alkaline mortar and carbonated concrete, calcium hydroxide crystals (and possibly cement paste) are dissolved due to hydroxyl ions being drawn by the electric field to the anode, while calcium ions are drawn to the cathode. As a result, calcium hydroxide dissolves at the interface. However, the observed amount of dissolved calcium hydroxide was lower than the theoretical amount calculated from Faraday's law and transport equations, and therefore it was suggested that other less visible species may have contributed to the current or that diffusion may have reduced the amount of transport in carbonated concrete.

Indeed, results obtained from the present tests show that on the carbonated reference specimen, where transport phenomena were not driven by the current, hydroxyl ions moved in opposite direction, i.e. from the mortar towards the carbonated concrete. This occurred also, although to a less extent, on specimens that were subjected to a low applied current, as well as on specimens that were analysed after 2 and 6 years of application of CP [12,17]. The net transport of hydroxyl ions is determined by two contrasting driving forces: the electric field due to the applied cathodic current, that tends to draw them towards the anode, and the gradient of concentration, that tends to draw them towards carbonated concrete. When no external current is applied, the gradient of concentration dominates and diffusion of alkalinity occurs from the mortar towards carbonated concrete. When an external current is applied, the distribution of alkalinity depends on the intensity of the applied current and on the time of application. This is schematically depicted in Figure 9. As a matter of fact, specimens subjected to CP with low applied current showed both phenomena, however the diffusion of alkalinity from the mortar towards carbonated concrete was localised at the interface with coarse aggregates, where the local current density was lower due to the low porosity of aggregates compared to cement paste, while the reduction of pH in mortar mainly occurred at the interface with cement paste. However, other factors may have affected transport phenomena, such as the presence of other ions in the concrete or mortar. Further tests will be carried out to investigate more in depth transport phenomena that can contribute to pH modifications.

What clearly emerged from the results is that the pH reduction in the mortar showed a progressive trend that was affected by the intensity of the applied current and time. Figure 10 plots the average thickness of the layer with reduced pH in mortar as a function of the charge density circulated across the mortar/concrete interface, i.e. the product of the current density and the time of application. In spite of the scatter of results, an increasing trend clearly emerged, as it is typical of electrochemical phenomena related to current circulation [23]. The presence of a threshold value of circulated charge under which the thickness was nil can be interpreted considering that phenolphthalein indicator can only highlight pH reductions to values lower than 9, which means that pH reductions to values higher than 9 cannot be detected in this way. This is probably the reason why microscopic observations carried out after 6 years highlighted an increased porosity, but no pH reduction in the mortar was detected (as it is indicated in Figure 10). This also implies that, provided pH reductions can be attributed to a mechanism of hydroxide dissolution, as previously proposed, phenolphthalein indicator can only detect it at an advanced stage. The intrinsic limitations of an indicator test are somewhat compensated by its immediacy in detecting hydroxyl ions.

Given the progressive increase of the thickness of mortar with reduced alkalinity, pH modifications due to the circulating current, which are initially localised at the interface with concrete, extend in the mortar towards higher depths. When the depth is such to include the anode

mesh, no more hydroxyl ions are available to compensate for the production of acidity and dissolution of mortar in contact with anode mesh begins to take place, as it was indicated by the presence of macrovoids around anode wires embedded in non-alkaline mortar. Possible consequences of these phenomena at the macroscopic scale, e.g. reduction of adhesion between anode mortar and concrete or increase of resistivity, will be investigated since they may affect the CP current circulation and the overall performance of the CP system.

The results obtained from the tests presented in this paper may be relevant not only for carbonated concrete structures, but also for structures exposed to chloride bearing environments, where a layer of carbonated concrete may be present on the external surface, as well as for CP applied with localised anodes (either with impressed current or sacrificial [24,25]), where the high current density at the anode may enhance chemical and microstructural modifications related to applied current.

In conclusion, the findings that were presented in this paper may be useful for a better understanding of factors affecting the performance of CP systems. Although so far no detailed quantitative information can be provided, it seems that possible deterioration phenomena at the anode may be hindered by embedding the anode mesh in an adequate layer of alkaline mortar and keeping the current supplied by the anode itself at the least value necessary to protect steel from corrosion.

Conclusions

Reinforced carbonated concrete slabs subjected to cathodic protection for about 13 years were analysed with a pH indicator to distinguish areas with high alkalinity (pH higher than 9) from almost neutral areas (pH lower than 9).

Next to the well known effect of realkalisation of initially carbonated concrete around steel bars, that was beneficial for corrosion protection, a pH reduction was detected in the anode mortar in contact with carbonated concrete. This is consistent with a mechanism of dissolution of calcium hydroxide (and possibly other alkaline components of the cement paste) that had been previously proposed based on microscopy observations, though it had not been observed as a macroscopic reduction of pH even on the same specimens after 6 years of CP application.

The pH reduction of the mortar was a progressive phenomenon whose extent was related to the charge circulated through the mortar itself, i.e. the product of the current density and the time of application; however, also the composition of the concrete and mortar seemed to play a role, and this aspect needs to be better investigated and quantified.

When the anode system is in contact with carbonated concrete, phenomena related to anodic acidification are initially localised at the interface with carbonated concrete and only at a later stage at the interface with the anodic mesh. A better understanding of the transport phenomena involved is necessary in order to characterise possible deterioration phenomena that may affect the performance of the anodic system on the long term.

References
[1] Angst UM, Hooton RD, Marchand J et al (2012) Present and future durability challenges for reinforced concrete structures, Mater Corros 63(12):1047-1051. doi: 10.1002/maco.201206898.
[2] Bertolini L (2008) Steel corrosion and service life of reinforced concrete structures, Struct Infrastruct Eng 4(2): 123-137. doi:10.1080/15732470601155490.
[3] Bertolini L, Elsener B, Pedeferri P, Redaelli E, Polder R (2013) Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair 2nd edn. Wiley-VCH, Weinheim. doi: 10.1002/9783527651696.

[4] Lollini F, Redaelli E, Bertolini L (2012) Analysis of the parameters affecting probabilistic predictions of initiation time for carbonation-induced corrosion of reinforced concrete structures, Mater Corros 63(12):1059-1068. doi: 10.1002/maco.201206720.

[5] Polder RB, Peelen WHA, Courage WMG (2012) Non-traditional assessment and maintenance methods for aging concrete structures – Technical and non-technical issues, Mater Corros 63(12):1147-1153. doi: 10.1002/maco.201206725.

[6] Bertolini L, Carsana M, Gastaldi M, Lollini F, Redaelli E (2011) Corrosion assessment and restoration strategies of reinforced concrete buildings of the cultural heritage, Mater Corros 62(2):146-154. doi: 10.1002/maco201005773.

[7] Redaelli E, Carsana M, Gastaldi M, Lollini F, Bertolini L (2011) Electrochemical techniques for the repair of reinforced concrete suffering carbonation-induced corrosion, Corros Rev 29(5-6):179-190. doi: 10.1515/CORRREV.2011.008.

[8] Pedeferri P (1996) Cathodic protection and cathodic prevention, Constr Build Mater 10(5):391-402.

[9] Glass GK and Buenfeld NR (1995) On the current density required to protect steel in atmospherically exposed concrete structures, Corros Sci 37(10):1643-1646.

[10] Glass GK, Hassanein AM, Buenfeld NR (1997) Monitoring the passivation of steel in concrete induced by cathodic protection, Corros Sci 39(8):1451-1458.

[11] Bertolini L, Bolzoni F, Pedeferri P, Lazzari L, Pastore T (1998) Cathodic protection and cathodic prevention in concrete: principles and applications, J Appl Electrochem 28(12):1321-1331.

[12] Bertolini L, Pedeferri P, Redaelli E, Pastore T (2003) Repassivation of steel in carbonated concrete induced by cathodic protection, Mater Corros 54(3):163-175. doi: 10.1002/maco.200390036.

[13] Glass GK, Page CL, Short NR (1991) Factors affecting the corrosion rate of steel in carbonated mortars, Corros Sci 32(12):1283-1294.

[14] Polder RB, Peelen WHA, Lollini F, Redaelli E, Bertolini L (2009) Numerical design for cathodic protection systems for concrete, Mater Corros 60(2):130-136. doi: 10.1002/maco.200805056.

[15] Polder RB, Leegwater G, Worm D, Courage W (2014) Service life and life cycle cost modelling of cathodic protection systems for concrete structures, Cement Concrete Comp. doi: 10.1016/j.cemconcomp.2013.05.004.

[16] Xia J and Li L-Y (2013) Numerical simulation of ionic transport in cement paste under the action of externally applied electric field, Constr Build Mater 39:51-59. doi: 10.1016/j.conbuildmat.2012.05.036.

[17] Polder R, Nijland T, Peelen W, Bertolini L (2002) Acid formation in the anode/concrete interface of activated titanium cathodic protection systems for reinforced concrete and the implications for service life. In: Proc. 15th International Corrosion Congress, Granada 22-27 September 2002. Spanish Council for Scientific Research, Madrid, pp 1-8.

[18] Peelen WHA, Polder RB, Redaelli E, Bertolini L (2008) Qualitative model of concrete acidification due to cathodic protection, Mater Corros 59(2):81-89. doi: 10.1002/maco.200804106.

[19] Bertolini L, Bolzoni F, Pastore T, Pedeferri P (2004) Effectiveness of a conductive cementitious mortar anode for cathodic protection of steel in concrete, Cement Concrete Res 34(4):681-694. doi: 10.1016/j.cemconres.2003.10.018.

[20] Mudd CJ, Mussinelli GL, Tettamanti M, Pedeferri P (1988) Cathodic protection of steel in concrete, Mater Performance 27(9):18-24.

[21] Pastore T, Pedeferri P, Mussinelli GL, Tettamanti M (1990) New developments in anode materials and monitoring systems for cathodic protection of steel in concrete. In: Proc. 11th International Corrosion Congress, Vol. 2, Firenze 2-6 April 1990, pp 467-472.

[22] Anstice DJ, Page CL, Page MM (2005) The pore solution phase of carbonated cement pastes, Cement Concrete Res 35:377-383. doi: 10.1016/j.cemconres.2004.06.041.

[23] Newman JS (1991) Electrochemical Systems 2nd edn. Prentice Hall, Englewood Cliffs.

[24] Redaelli E, Lollini F, Bertolini L (2013) Throwing power of localised anodes for the cathodic protection of slender carbonated concrete elements in atmospheric conditions, Constr Build Mater 39:95-104. doi: 10.1016/j.conbuildmat.2012.05.014.

[25] Redaelli E, Lollini F, Bertolini L (2014) Cathodic protection with localised galvanic anodes in slender carbonated concrete elements, Mater Struct. doi: 10.1617/s11527-013-0154-x.

Tables

Table 1 Description of specimens and tests. I = current applied between anode and reinforcement; CD = current density referred to the surface of steel, mortar and activated titanium anode mesh

Specimen	Concrete	I (mA)	CD (mA m^{-2}) Steel	CD (mA m^{-2}) Mortar	CD (mA m^{-2}) Anode	Duration (y)
12	Carbonated	0.5	10	4.2	18	13.25
13	Carbonated	0.25	5	2.1	9	13.25
22	Carbonated + 0.4% Cl$^-$	0.5	10	4.2	18	13.25
23	Carbonated + 0.4% Cl$^-$	0.25	5	2.1	9	13.25
16	Carbonated	0.5	10*	4.2	18	11.8
15	Carbonated	0.25	5*	2.1	9	11.8
25	Carbonated + 0.4% Cl$^-$	0.5	10*	4.2	18	11.8
18-19	Carbonated	1	10	8.3	36	11.76
26-27	Carbonated + 0.4% Cl$^-$	1	10	8.3	36	11.68
1	Alkaline	-	-	-	-	13.37
11	Carbonated	-	-	-	-	13.37
21	Carbonated + 0.4% Cl$^-$	-	-	-	-	13.37

* previously fed with 2 mA m^{-2} for 1.37 year and with 70 mA m^{-2} for 1 month (current densities are referred to steel)

Table 2 Thickness of the layer with pH lower than 9 in mortar adjacent to carbonated concrete

| Specimen	Concrete	Average thickness (min-max) (mm)
12	Carbonated	1.32 (0.63-1.9)
13	Carbonated	0.73 (0-2.2)
22	Carbonated + 0.4% Cl$^-$	1.74 (1.3-2.5)
23	Carbonated + 0.4% Cl$^-$	0.37 (0-1.1)
16	Carbonated	1.47 (1.1-2.2)
15	Carbonated	0.69 (0-1.25)
25	Carbonated + 0.4% Cl$^-$	1.22 (0-2.2)
18-19	Carbonated	1.53 (0-3.3) (anode system) 0.38 (0-1.1) (joining mortar)
26-27	Carbonated + 0.4% Cl$^-$	3.1 (1.9-5) (anode system) 1.2 (0.63-2.5) (joining mortar)
1	Alkaline	0
11	Carbonated	0
21	Carbonated + 0.4% Cl$^-$	0

Captions for figures
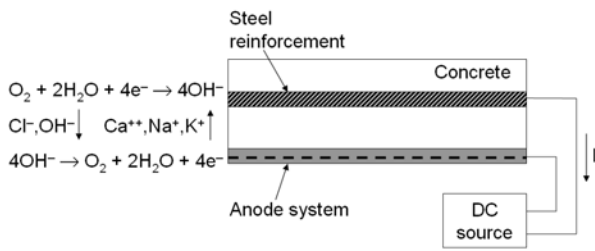
Fig. 1 Application of cathodic protection to reinforced concrete with indication of main electrochemical reactions and transport phenomena involved
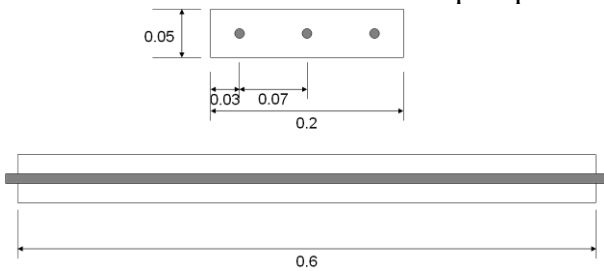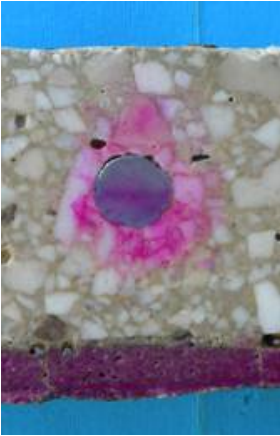

Fig. 2 Basic geometry of reinforced concrete specimens (dimensions in m)
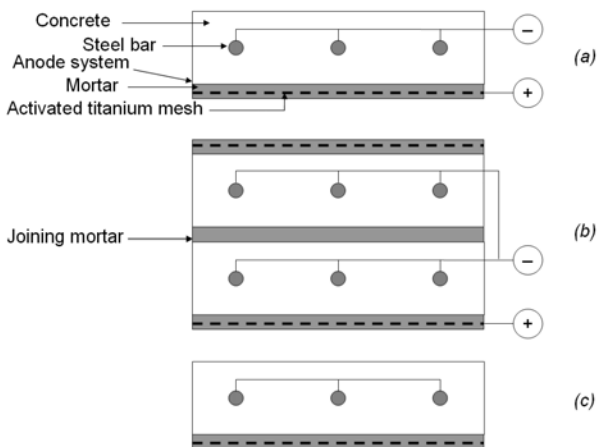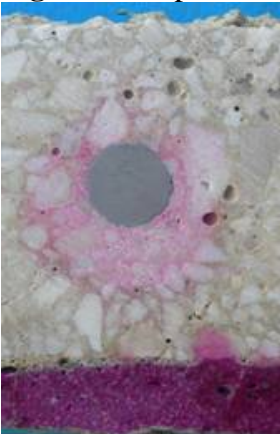

Fig. 3 Representation of experimental tests: *(a)* single specimens subjected to CP tests at 5 and 10 mA m^{-2}, *(b)* "*sandwich*" specimens subjected to CP tests at 10 mA m^{-2} and *(c)* reference specimens
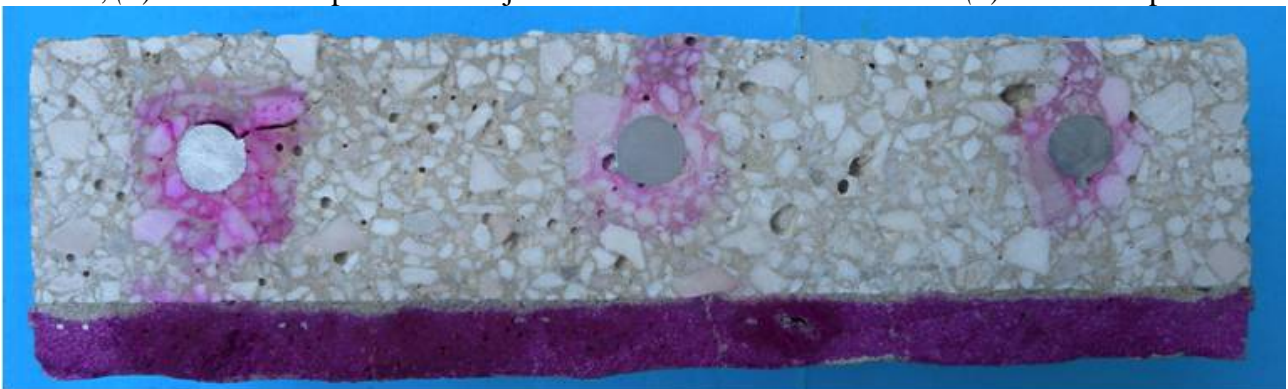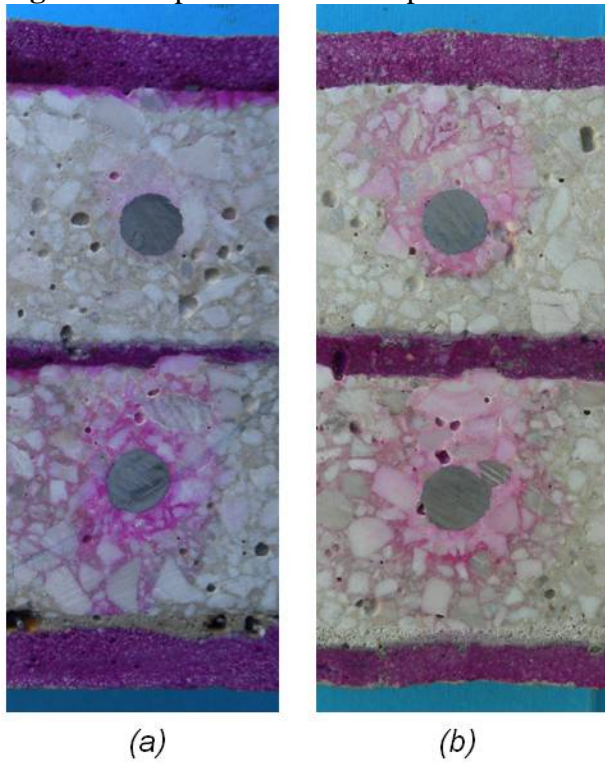

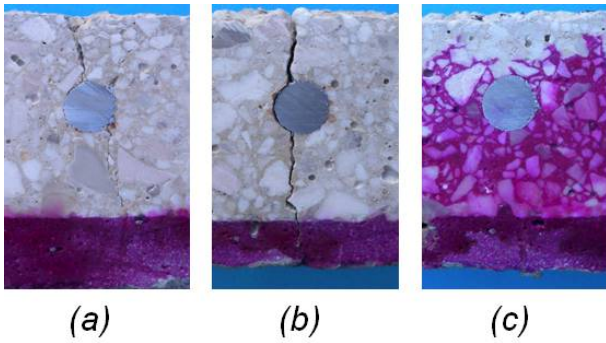**Fig. 4** Phenolphthalein test on cut section of specimen 12
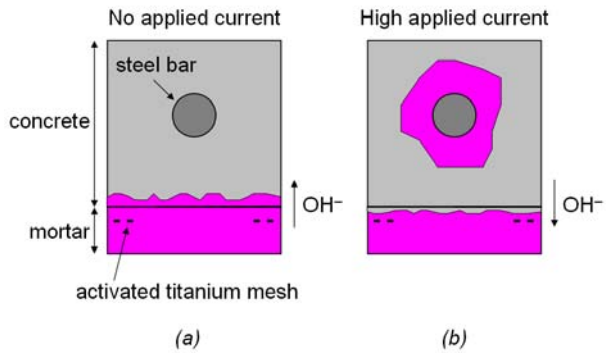
Fig. 5 Phenolphthalein test on specimen 22

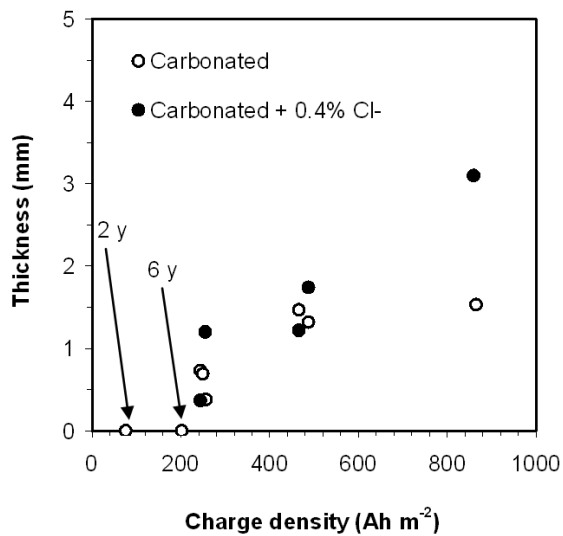

Fig. 6 Phenolphthalein test on specimen 13

(a) (b)

Fig. 7 Phenolphthalein test on specimens 18-19 *(a)* and 26-27 *(b)*

Fig. 8 Phenolphthalein test on specimens 11 *(a)*, 21 *(b)* and 1 *(c)*

Fig. 9 Movement of hydroxyl ions at the interface between mortar and carbonated concrete under concentration gradient *(a)* and electric field *(b)*

Fig. 10 Thickness of layer with pH lower than 9 on mortar applied to carbonated and carbonated with chlorides concrete specimens, as a function of the circulated charge. 2 y and 6 y refer to results of phenolphthalein tests obtained in the early stage of tests