Resistance to carbonation of concrete after realkalisation by absorption of sodium carbonate solution

Elena Redaelli*, Luca Bertolini Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "G. Natta" *corresponding author Address: via Mancinelli 7, 20131, Milan, Italy Tel: +39 02 2399 3115 E-mail: elena.redaelli@polimi.it

Abstract

The paper presents an experimental research on the durability of a non-conventional technique for the repair of reinforced concrete damaged by carbonation-induced corrosion of steel reinforcement. The technique is called electrochemical re-alkalisation and is often considered as an option for the repair of buildings, structures and other artefacts made of reinforced concrete, for which conservation requirements are becoming increasingly important, in spite of their relatively young age. Absorption of a sodium carbonate solution is one of the processes that leads to concrete realkalisation. The aim of the work is to investigate the long-term ability of re-alkalised concrete to contrast future carbonation. Concrete specimens with six different compositions were initially carbonated, then re-alkalised through absorption of a sodium carbonate solution, and then exposed again to carbonation (re-carbonation). The results showed that the pH of concrete after recarbonation was only slightly lower compared to that of re-alkalised concrete, highlighting a contribution of the treatment in contrasting future pH reduction.

Keywords

Carbonation; Corrosion; Durability; Electrochemical technique; Modern architecture; Realkalisation; Reinforced concrete; Repair.

Introduction [heading]

Today many reinforced concrete buildings, structures and other artefacts that were built throughout the XX century have reached the end of their service life and need interventions of extraordinary maintenance. One of the main deterioration phenomena is the corrosion of steel reinforcement due to concrete carbonation, which is a natural reaction occurring between carbon dioxide in the atmosphere and the alkaline components of the hydrated cement paste. Carbonation is a progressive reaction that neutralises the alkalinity of concrete: when it reaches the depth of the concrete cover, steel reinforcement is no longer protected from corrosion and, in the presence of oxygen and humidity, it actively corrodes, producing stains of rust, spalling and delamination of concrete cover.

Depending on the extent of damage and environmental aggressiveness, conventional methods of repair may imply replacement of carbonated concrete, reconstruction with commercial repair mortars and application of paintings and coatings as a protection towards further ingress of carbon dioxide and humidity. However, such interventions may be inappropriate if the original nature of the materials, their shape and surface texture need to be preserved due to the cultural, historical or architectural value of the artefact (Brocklebank, 2005). Examples include reinforced concrete buildings of modern architecture (including churches), structures of historical industrial sites, decorative artefacts and facades of residential buildings. If conservation requirements need to be taken into account, non-conventional techniques of intervention should be used, aimed not only at restoring the safety and serviceability, but also at respecting the integrity of materials and surfaces (De Jonge, 1997; Bertolini et al., 2011; Redaelli et al., 2011).

Alternative methods of intervention are available that allow to preserve as much as possible the original concrete material and its texture. Among these, electrochemical realkalisation (*ER*) has often been reported to be particularly suitable for reinforced concrete buildings and structures to be preserved. *ER* is an electrochemical technique based on the application of a cathodic current to the steel reinforcement (Mietz, 1998; Bertolini et al., 2012). Unlike other electrochemical techniques, such as for instance cathodic protection, *ER* is a temporary treatment and so it does not require a permanent anode system that would considerably affect the surface of concrete. *ER* relies on a twofold mechanism: the production of alkalinity at the interface between reinforcement and concrete and the ingress of an alkaline solution (usually of sodium carbonate) in which the anode is immersed. Since mechanically sound concrete, although carbonated, can be left in place, *ER* allows to maximise concrete preservation, protecting in the meantime steel from corrosion.

The effectiveness of the *ER* treatment in controlling reinforcement corrosion has been discussed by several researchers (Mietz, 1995; Yeih & Chang, 2005; Miranda et al., 2006; Redaelli & Bertolini,

2011; Tong et al., 2012; Redaelli et al., 2014); conversely, the contribution to realkalisation related to the penetration of the alkaline solution has received less attention in the scientific literature (Banfill, 1997; Van den Hondel & Polder, 2001; Franzoni et al., 2014), in spite of being often claimed to contribute to the overall durability of the treatment.

Although *ER* was introduced in the 1980s and since then it was characterised by means of a number of laboratory tests, its application is not widespread and field data on its effectiveness and durability are relatively few (Velivasakis et al., 1998; Bertolini et al., 2008; Bertolini et al., 2010). To this regard, a key aspect is the ability of the absorbed alkaline solution to contrast future carbonation after re-exposure to the atmospheric environment, in particular if a protective coating or painting shall not be applied. To this regard, this paper aims at providing a contribution for a better understanding of the resistance to re-carbonation of concrete after re-alkalisation due to the penetration of alkaline solution.

Carbonated specimens made of concrete with six different compositions were re-alkalised through absorption of an alkaline solution of sodium carbonate, in order to simulate the re-alkalisation due to penetration of the solution occurring during the *ER* treatment. Afterwards, the specimens were re-carbonated and the penetration of carbonation was compared with that obtained on the initially alkaline concrete, in order to study the effectiveness of *ER* treatment in preventing concrete re-carbonation.

Experimental methods [heading]

Six different concrete compositions were considered. Concrete mixtures *A* through *D* were obtained with portland limestone cement and water/cement (w/c) ratios of 0.55 and 0.70, with and without addition of chlorides in amount of 0.4% with respect to cement mass (so as to simulate a mild contamination with chlorides); mixtures *E* and *F* were obtained with ground granulated blastfurnace slag cement and w/c ratios of 0.55 and 0.70. Detailed compositions are reported in Table 1 together with the main characteristics measured at fresh and hardened state of concrete.

Concrete cubes were cast with side of 100 mm. The cubes were wet cured for 7 days after casting, exposed to laboratory air for additional 7 days, and then subjected to accelerated carbonation at 100% CO_2 and 60% relative humidity (RH) for 3 months. During this period, the propagation of carbonation was measured on replicate sacrificial specimens. After this initial accelerated carbonation, the cubes were stored in laboratory for 7 years.

After this period of aging, each concrete cube was cut to obtain four prismatic specimens with nominal dimensions of 50 mm \times 50 mm \times 100 mm. Since phenolphthalein test showed that concrete was not fully carbonated, the specimens were further exposed to 100% CO₂ for about a month, until complete carbonation. Prismatic specimens were labelled with a letter indicating the concrete composition and a progressive number from 1 to 4 and they were masked with epoxy except on two parallel faces, so that transport phenomena could occur only through them. Specimens preparation and sequence of tests are schematically shown in Figure 1.

Re-alkalisation of initially carbonated specimens [sub-heading]

The *re-alkalisation* of carbonated concrete prisms was done through a capillary absorption test, which also allowed characterising the kinetics of absorption, followed by complete immersion and vacuum saturation in the test solution.

The capillary absorption test was performed according to EN standard 13057, using an alkaline solution of sodium carbonate (Na₂CO₃ 1M) as test solution. This solution is normally used as anodic solution in the electrochemical realkalisation treatment. The specimens were dried in a climatic chamber at 20°C and 50% RH and their masses were recorded. They were positioned in a tray containing the test solution so that only the bottom surface was in contact with the solution. For each concrete composition, three specimens (1, 2 and 3) were tested with the alkaline solution and one specimen (4) was kept as reference and tested with water. The amount of absorbed solution was obtained by measuring the mass increase of the specimens after 12 min, 30 min, 1 h, 2 h, 4 h, 24 h, 48 h and 72 h. Afterwards, the specimens were completely immersed in the test solution under vacuum. When the mass increase in 24 h was lower than 0.1%, the specimens were deemed saturated. The re-alkalisation of the specimen, perpendicular to the bare surfaces, and performing phenolphthalein test on the cutting surface, as it will be described later.

Re-carbonation [sub-heading]

After drying in laboratory air for a month, re-alkalised specimens were subjected to a further treatment of carbonation, that will be indicated with *re-carbonation* to distinguish it from the carbonation of the initially alkaline concrete. In particular, for each type of concrete, two specimens (1 and 2) were exposed to accelerated re-carbonation in a chamber with 100% CO_2 and one specimen (3) was exposed to natural re-carbonation (outdoor environment sheltered from the rain).

The penetration depth of accelerated carbonation was evaluated after 28 and 90 days. The penetration depth of natural carbonation was evaluated after 90 days.

pH measurements [sub-heading]

The initial carbonation of concrete as well as the subsequent advancements of re-alkalisation and recarbonation were checked by cutting a thin slice from each specimen, perpendicularly to the exposed surfaces, and spraying the freshly cut surface with an alcoholic solution of phenolphthalein. Phenolphthalein is a pH indicator that turns pink for pH values higher than 9 and remains colourless for pH values lower than 9.

Owing to the uncertainties in detecting the re-alkalisation and re-carbonation with phenolphthalein test, related to the low intensity of colouring of indicator, pH measurements were also carried out by dispersing concrete powders in distilled water and measuring the pH of the dispersion, according to the procedure described in Räsänen & Penttala, 2004. Powders were obtained by grinding concrete fragments collected from originally alkaline concrete (indicated with a), carbonated concrete (c), re-alkalised concrete (ra) and re-carbonated concrete (rc). The dispersions were prepared by adding 5 g of powder to 10 g of distilled water and mixing with a magnetic stirrer for 10 min. After 2 min of settling, a pH probe was inserted in the liquid and the pH was measured with a calibrated digital pH-meter.

Results and discussion [heading]

Characterisation of materials [subheading]

Figure 2 shows the advancement of accelerated carbonation that was measured on the alkaline sacrificial cubes exposed to 100% CO₂ and Figure 3 shows the coefficient of carbonation $K_{\text{acc,alk}}$ that was obtained by interpolation through the relation:

(1)
$$C = K_{acc,alk} \cdot \sqrt{t}$$

where *C* is the depth of carbonated concrete (i.e. concrete with pH<9 according to phenolphthalein test) and *t* is the time of exposure to the accelerated carbonation environment (Neville, 1995). $K_{\text{acc,alk}}$ ranged from 25-30 mm/y^{0.5} for concretes *A* and *B* to 60-70 mm/y^{0.5} for concretes *C* through *F*. These value are representative of the rate of carbonation in accelerated conditions, and can be used for comparative purpose amongst the various compositions considered (but not for estimating the carbonation rate in natural conditions). In particular, a clear distinction emerged between the

behaviour of concretes *A* and *B*, that were made with limestone cement and w/c ratio of 0.55, and the rest of the concretes, that were made either with limestone cement and w/c of 0.70 or with slag cement: the former showed a higher resistance to carbonation compared to the latter. It is well known that the resistance to carbonation is higher for concrete with low w/c ratio, due to the lower porosity, and lower for concrete containing pozzolanic or hydraulic additions, due to the lower amount of available calcium hydroxide (Parrott, 1992; Ngala & Page, 1997; Bertolini et al., 2009b).

The tests of capillary absorption with alkaline solution, to which the concrete prisms were subjected after the aging period and complete carbonation and which were aimed at promoting the realkalisation of initially carbonated concrete, allowed to characterise the various concretes in terms of other parameters related to durability, such as the coefficient of sorptivity and the estimated porosity.

Figure 4 shows an example of the results of capillary absorption tests that were obtained on concrete *A*. For each concrete specimen, the amount of absorbed liquid was referred to the absorption surface and plotted as a function of the square root of time. An approximately linear increasing trend was observed, indicating that absorption is a progressive phenomenon with decreasing rate as a function of time. Overall, the results showed a small scatter. The plots were interpolated to determine the coefficient of sorptivity S_{carb} , which was calculated as:

(2)
$$S_{carb} = \frac{\Delta m_{24h}}{s \cdot \sqrt{24}}$$

where Δm_{24h} is the mass of test solution absorbed after 24 h and *s* is the absorption surface area. The results obtained on all concretes are summarised in Figure 5. S_{carb} ranged from values around 0.3-0.5 kg/m² h^{0.5} for concretes *A* and *B*, to values around 0.8 kg/m² h^{0.5} for concretes *C* and *D* and values around 0.75 and 1.1 kg/m² h^{0.5} for concretes *E* and *F*. No substantial differences emerged between S_{carb} values obtained with alkaline solution of sodium carbonate and values obtained with water.

The coefficient S_{carb} is a measure of the initial rate of capillary absorption when dry concrete gets in contact with the liquid. It is mainly related with the concrete porosity, in terms of total volume of pores and pore size distribution (Vos, 1971). Overall, the values obtained are representative of quite dense materials: as a comparison, typical values of the coefficient of sorptivity are 25 kg/m² h^{0.5} for fired-clay brick and 6 kg/m² h^{0.5} for cement-lime masonry mortar (Bertolini et al., 2009a; Hall & Hamilton, in press). Both carbonation and aging period, as well as the initial wet curing, to which the concrete specimens were subjected, contributed to promote a fine pore structure and, hence, to

reduce the coefficient of sorptivity of concrete even for the highest w/c ratio of 0.70 (Ngala & Page, 1997; Dias, 2000).

The coefficient of absorption W_{carb} was determined as:

(3)
$$W_{carb} = \frac{m_{carb,sat} - m_{carb,dry}}{m_{carb,dry}} \cdot 100$$

where $m_{carb,sat}$ is the mass of the specimen after vacuum saturation in the test solution and $m_{carb,dry}$ is the mass of the dry specimen. The results obtained are reported in Figure 6. W_{carb} was about 3.6-4% for concretes *A* and *B* and 5% for concretes *C* and *D*; concretes *E* and *F* showed values of 5-5.9% and 5.3-5.9% respectively. A slight systematic increase was observed for W_{carb} values obtained with the sodium carbonate solution compared to those obtained with water, which is merely due to the higher density of sodium carbonate solution (1.1 g/cm³) compared to water (1 g/cm³). The coefficient of absorption is a measure of the amount of solution that can be contained in the open and interconnected pores of the material. The values of absorption are again representative of concrete with relatively low porosity: typical values are 20% for fired-clay brick and 15% for mortar. If all the pores are open and interconnected, as it usually occurs for porous construction materials, the coefficient of absorption is related to the porosity P_{carb} through:

(4)
$$W_{carb} = \frac{V_p \cdot \rho_{liquid}}{V_{tot} \cdot \rho_{bulk}} \cdot 100 = P_{carb} \cdot \frac{\rho_{liquid}}{\rho_{bulk}}$$

where V_p is the volume of the open pores, V_{tot} is the total volume (solid + pores), ρ_{liquid} is the density of the saturating liquid and ρ_{bulk} is the apparent density of the dry material. The volume porosity of carbonated concrete ranged from 8% for concrete A to 14% for concrete F (Figure 7).

On the whole, comparing the various carbonated concretes, the results showed that, for a given type of cement, lower values of S_{carb} , W_{carb} and P_{carb} were obtained for w/c ratio of 0.55 and higher values were obtained for w/c ratio of 0.70: for instance for limestone portland cement W_{carb} was 3.6% for w/c of 0.55 (concrete A) and 4.9% for w/c of 0.7 (concrete C). The cement type also affected the results: for instance, for w/c of 0.70 W_{carb} was 4.9% for portland limestone cement (concrete C) and 5.9% for slag cement (concrete F). Conversely, the addition of 0.4% chlorides in the concrete did not affect the parameters S_{carb} , W_{carb} and P_{carb} . Except for variations of such parameters related to their compositions, all the concretes can be considered as well aged and with low permeability, in spite of their young age and relatively high values of w/c ratio, and they can be considered representative of historical concretes encountered in existing buildings and structures.

Finally, Table 2 shows the results of phenolphthalein tests that were obtained on concrete after the absorption and immersion in sodium carbonate solutions. The pink colouring of the indicator is rather weak and even hard to detect, in particular compared to that usually obtained on originally alkaline concrete (an example is shown for comparison for concrete F in Figure 8). Moreover, in spite of the vacuum saturation procedure with the alkaline solution of sodium carbonate, the section of the prisms was not fully realkalised, as indicated by areas with pH lower than 9 far from the absorption surfaces. This indicates that the penetration of the alkaline solution of sodium carbonate in a good-quality, mechanically sound and carbonated concrete by means of a simple absorption mechanism is a relatively slow process that allows to realkalise only few millimetres of concrete. To this regard, it should be reminded that the application of ER to reinforced concrete relies on an external current that not only gives the main contribution to the production of alkalinity through the cathodic reaction at the steel reinforcement, but also contributes to promote the ingress of alkaline solution. Although in the present work the penetration of the alkaline solution could not be forced by an applied current, it was assumed that the concrete soaked with the solution was equivalent to that achieved after an *ER* treatment, except for the rate of penetration that was lower for the former compared to the latter. Hence, with regard to the resistance to future re-carbonation, the concrete specimens re-alkalised through simple absorption were considered representative of real concrete subjected to ER treatment.

Resistance to re-carbonation [subheading]

As it was shown in the previous section, phenolphthalein test showed the presence of a layer of pink-coloured concrete next to the outmost surfaces of all the specimens, which was indicative of absorption of the alkaline solution of sodium carbonate, and as a consequence the specimens were used to measure the resistance provided by this layer to a further process of carbonation, in both accelerated and natural conditions. The results are shown in Table 2. Again, the outmost surfaces of all specimens showed a pink colour, with no evidence of colourless areas. This indicates that after re-carbonation, both in accelerated and natural conditions, the pH remained higher than 9, i.e. the turning point of phenolphthalein indicator.

Since pH indicators can only provide a qualitative range of pH, an attempt was done to quantify pH by means of water-suspensions of powdered concrete. Figure 9 reports the results obtained on the various concretes. Alkaline specimens were only available for concretes E and F and their pH was around 12.4-12.5. Carbonated concrete showed pH values between 8.5 and 9, regardless of the concrete composition. Re-alkalised concrete had pH between 10.5 and 10.7, i.e. an intermediate

value between carbonated and alkaline concrete and slightly lower than the pH of the alkaline solution of sodium carbonate which was around 11.6-12. Finally, re-carbonated concrete showed pH values between 10.1 and 10.5, again regardless of the concrete composition. Hence, a slight pH decrease occurred passing from re-alkalised concrete to re-carbonated concrete (on average from 10.6 to 10.3), however it was much smaller than that occurred passing from alkaline to carbonated concrete (on average from 12.4 to 8.9). Although measuring the pH of concrete is not an easy task and its results may be affected by the methodology (Grubb et al., 2007; Alonso et al., 2011; Wan et al., 2013), the obtained pH values can be used to discuss the pH variations that occurred in the concrete specimens as a result of the cycles of carbonation / re-alkalisation / re-carbonation to which they were subjected.

The initial carbonation of alkaline concrete is a well-known phenomenon which is mainly related to the reaction of carbon dioxide with the alkaline components of the cement paste, in particular calcium hydroxide crystals that constitute the alkalinity reservoir for concrete (Neville, 1995). The process of carbonation consumes calcium hydroxide crystals, that are no longer available in carbonated concrete (Chang & Chen, 2006; Villain et al., 2007). The subsequent absorption of alkaline solution into carbonated concrete implies the saturation of the open and interconnected pores with the solution itself. In the absence of a detailed description of possible interactions between the solution and the cement paste constituents, it can be assumed that the contribution to re-alkalisation is only related to the presence of the solution itself. As a consequence, the recarbonation of concrete will involve different mechanisms compared to initially alkaline concrete: although no specific data are available in the literature, it can be assumed that the alkalinity of the solution that is contained in the concrete pores will be neutralised by carbon dioxide and, given its buffering ability, it is expected to contrast the reduction of pH due to the penetration of carbon dioxide from the atmosphere. Another possible mechanism is related with the precipitation of carbonates in the pores and subsequent reduction of the porosity. In both cases the alkalinity reservoir for concrete will be provided by the alkaline solution absorbed inside its pores.

On the whole, the results of phenolphthalein test and pH measurement after re-carbonation indicated that the alkalinity related with the absorption of alkaline solution of sodium carbonate was mainly retained in both accelerated and natural conditions of carbonation. This indicates that the surface of a concrete element subjected to *ER* treatment, where a re-alkalisation contribution due to absorption of alkaline solution occurs, may contribute to contrast future pH reduction thanks to the absorption of the alkaline solution itself.

Conclusions [heading]

Concrete specimens with six different compositions were characterised in terms of initial resistance to carbonation and other durability-related properties in the carbonated state such as: sorptivity, absorption and porosity. The results obtained indicated that, in spite of their relatively young age, these materials could be considered representative of historical concretes that may be present in existing building and structures, thanks to the carbonation process and the period of aging to which they were subjected.

Their resistance to re-carbonation after re-alkalisation was evaluated in accelerated (100% CO₂) and natural condition. Phenolphthalein indicator did not give evidence of areas with pH lower than 9, indicating that the alkalinity achieved due to absorption of alkaline solution was substantially maintained. Also the measurement of pH of concrete powder suspensions highlighted that only a slight decrease of pH occurred passing from re-alkalised concrete (around 10.6) to re-carbonated concrete (around 10.3). The resistance to re-carbonation was attributed to the alkalinity of the absorbed solution and to its amount, as well as the buffering ability of sodium carbonate. Hence, the re-alkalisation contribution due to the penetration of the alkaline solution of sodium carbonate that occurs during *ER* treatment may contribute to contrast future pH reduction.

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Tables

Concrete	А	В	С	D	Е	F	
w/c ratio	0.55	0.55	0.70	0.70	0.55	0.70	
Cement type	Portland limestone cement				Slag cement		
Mixed-in 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 aggregate (kg/m ³)	1800	1800	1872	1872	1800	1872	
Calcium chloride CaCl ₂ ·2H ₂ O (kg/m^3)	-	2.99	-	2.36	-	-	
Acrylic type super- plasticiser (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	
Chlorides (% mass concrete)	0.01	0.06	0.01	0.05	0.03	0.03	

Table 1 Composition and early-age properties of concrete mixtures.

Table 2 Results of phenolphthalein tests highlighting areas with pH > 9 (pink) on the various concretes after realkalisation and subsequent re-carbonation in accelerated and natural conditions.

Concrete	After re-alkalisation by absorption Na ₂ CO ₃ 1M	After accelerated re-carbonation (100% CO ₂ for 90 d)	After natural re-carbonation (outdoor sheltered for 90 d)
А			
В			
С			
D			
E			
F			

Figures



Figure 1 Schematic description of specimens and sequence of tests, for each concrete.



Figure 2 Depth of concrete with pH lower than 9 measured by means of phenolphthalein test on initially alkaline specimens as a function of square root of time during exposure to accelerated carbonation at 100% CO₂.



Figure 3 Coefficient of carbonation $K_{acc,alk}$ obtained in accelerated conditions (100% CO₂) on initially alkaline concrete specimens.



Figure 4 Example of results of capillary absorption test carried out on specimens made with concrete *A*.



Figure 5 Coefficient of sorptivity S_{carb} for carbonated concretes with various compositions, tested with sodium carbonate solution and water.



Figure 6 Coefficient of absorption W_{carb} for carbonated concretes with various compositions, tested with sodium carbonate solution and water.



Figure 7 Porosity P_{carb} as a function of coefficient of absorption W_{carb} for carbonated concrete of various compositions.



Figure 8 Example of phenolphthalein test on concrete *E* highlighting carbonated concrete (grey) and alkaline concrete (dark pink).



Figure 9 pH of suspensions of concrete powders for the various compositions.