

# The influence of hydrophobic surface coatings on carbonation induced corrosion in reinforced concrete structures

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Rebar corrosion is the main cause of deterioration in reinforced concrete structures and leading not only to problems regarding the user's safety but also to high costs for necessary repairs. Carbonation of concrete in contact with reinforcements leads to a uniform consumption of the rebars cross section, the formation of expansive corrosion products and thus cracking and spalling of the concrete cover. Hydrophobic pore lining treatments can be an interesting method to control the propagation of rebar corrosion in carbonated concrete and, thus, to prolongate the service life of the structures. In this paper, the effect of a hydrophobic coating on initiation and propagation of carbonation-induced corrosion was analysed.

**KEYWORDS:** CORROSION, REINFORCED CONCRETE STRUCTURES, CARBONATION-INDUCED CORROSION, SURFACE COATINGS, HYDROPHOBIC TREATMENT

## INTRODUCTION

In alkaline concrete, a passive film on the surface of the steel rebars is formed. As long as this layer is present, corrosion may not initiate. However, this film may break down due to the penetration of aggressive species such as CO<sub>2</sub> or chlorides into the concrete. The diffusion of CO<sub>2</sub> into the concrete leads to the neutralization of the pH of pore solution and thus to the depassivation of the rebars. In absence of the passive film and in the presence of water and oxygen the steel may then corrode. Besides the reduction in steel cross section, rebar corrosion causes cracking and spalling of the concrete cover, due to the formation of expansive corrosion products, as well as loss of bond strength between concrete and steel with a resulting effect on the safety of the structures [1]. In the design of reinforced concrete structures, it is to be assured that the target service life of the structure is reached. This may be achieved by adjusting parameters such as the concrete quality and cover thickness. In some specific condition (e.g. presence of harsh environmental condition, long service life, complexity in the maintenance activities ...) the application of additional preventative techniques such as the surface treatments can be a suitable solution to reach the required durability [2]. Surface treatments can be an effective solution also to control corrosion on existing structures. Different types of treatments are available, some that can reduce the penetration of the aggressive species, some

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that can reduce the corrosion rate after corrosion initiation and other that provide both effects [3]. Among the different concrete coatings, the hydrophobic treatments can reduce the internal humidity of the concrete, thus reducing the corrosion rate, and limit the penetration of the chloride, increasing the time for corrosion initiation. This coating consists, generally, of silanes or siloxanes which, applied to the concrete surface, creates an invisible film (a layer of molecular thickness) on the concrete and the superficial pore walls and turn concrete water-repellent increasing the contact angle between water and concrete [4]. The advantages of hydrophobic treatments are their invisibility, the easy use and application. The breathability of the concrete is not reduced by their use, because pores remain open, thus the drying of concrete is promoted [5]. In literature varying results are reported regarding the effect of hydrophobic treatments on the penetration of carbonation in concrete. It might be assumed that, due to the drying of the concrete, CO<sub>2</sub> diffusion is promoted [6], however, some researchers found an increase in CO<sub>2</sub> penetration re-

sistance [7] others, however, detected no effect compared to uncoated concrete [8]. This coating may suffer degradation phenomena (generally related to UV light, oxidation or freeze-thaw cycles [1]), thus its effectiveness over time has to be evaluated so as to schedule the maintenance and guarantee the durability of the structure.

This paper analyses the influence of the use of a new hydrophobic treatment (in gel form) on the prevention of carbonation induced corrosion. The effect of the coating on initiation (i.e. on the penetration of carbonation) and propagation (on the reinforcement corrosion rate and the concrete resistivity) of carbonation-induced corrosion are evaluated.

### EXPERIMENTAL PROCEDURE

Eighteen concrete samples were realised. The concrete (Tab.1) was prepared mixing 400 kg/m<sup>3</sup> of limestone cement (type CEM II/ A-L 42,5R), 260 l/m<sup>3</sup> of water (w/c ratio of 0.65) and 1606 kg/m<sup>3</sup> of aggregates (ϕ<sub>max</sub> = 9.5 mm).

**Tab.1** - Mix design of the concrete used - Mix design del calcestruzzo utilizzato.

Cement (kg/m <sup>3</sup> )	Water (l/m <sup>3</sup> )	Aggregates (kg/m <sup>3</sup> )	w/c ratio
400	260	1606	0.65

Sixteen unreinforced cubic samples, with a side length of 100 mm, were used for the determination of carbonation depth over time in natural (12 samples) and accelerated conditions (4 samples). Two prismatic reinforced samples (with dimension: 150x120x50 mm) were produced for the determination of corrosion propagation. In each of these samples, two reinforcements (length=150 mm, ϕ=10 mm) with a concrete cover of 10 mm were embedded. The rebars used are of the type B450C. They were sandblasted and cleaned with alcohol before casting. Electrical connections were realized on one side of the bar and both ends of the bar were insulated so as to obtain an exposed length of the rebar, in contact with concrete, of 80 mm. A reference electrode (activated titanium), placed close to the rebars, and two stainless steel wires (ϕ=2mm), positioned in the middle of the sample at a distance of 2 cm, were embedded. The wires are necessary in order to perform measurements of corrosion rate and electrical resistivity (determined measuring the conductance between the two

electrodes with an electrical conductivity meter - Delta OHM HD 2156.1)

After casting the cubic samples to be used for the natural exposure condition as well as the two prismatic samples were stored for 7 days in a curing chamber (R.H. > 95%, 23°C), the cubic samples for exposure to accelerated carbonation were cured for 21 days respectively. After curing, all samples were stored in laboratory conditions for 3 weeks. The prismatic samples were subsequently exposed to accelerated carbonation (60% R.H., 20°C, 3% CO<sub>2</sub>) for 147 days until the total carbonation of the sample. One of the faces, in contact with the formwork during casting, of half of the samples was then prepared, roughened with emery paper and cleaned with compressed air, and treated with a hydrophobic treatment (silane based) in gel form (4g of gel/ 100 cm<sup>2</sup>); in the prismatic sample, both faces 150x120 mm were treated with the coating. The other half of the samples was left uncoated. All the surfaces, except the treated ones and respectively one (in contact with the for-

network during casting) of the uncoated samples, of the cubic samples were subsequently coated by epoxy resin, so as to limit the penetration only to one face (test surface); in the prismatic samples only the lateral faces were coated with the epoxy resin. Twelve cubic samples were exposed to the atmosphere of Milano in order to compare natural carbonation in treated and untreated specimens. Of these samples, four (two treated and two untreated) were positioned in a sheltered condition and eight in unsheltered conditions. For the samples in unsheltered conditions half of them were exposed with the test surface in horizontal position, the others in vertical position. Furthermore, four cubic samples were placed in an accelerated carbonation chamber (60% R.H., 20°C, 3% CO<sub>2</sub>). The prismatic samples were exposed for about 2 years in unsheltered atmospheric conditions in Milano and, then, they were moved to a special chamber applying cycles of wetting (spraying of water), drying (air ventilation), IR and UV (280-400nm) radiation in order to simulate an accelerated natural exposure (2 hours of water spraying, 4 hours of air ventilation, 30 hours of exposure to IR radiation and 12 hours of exposure

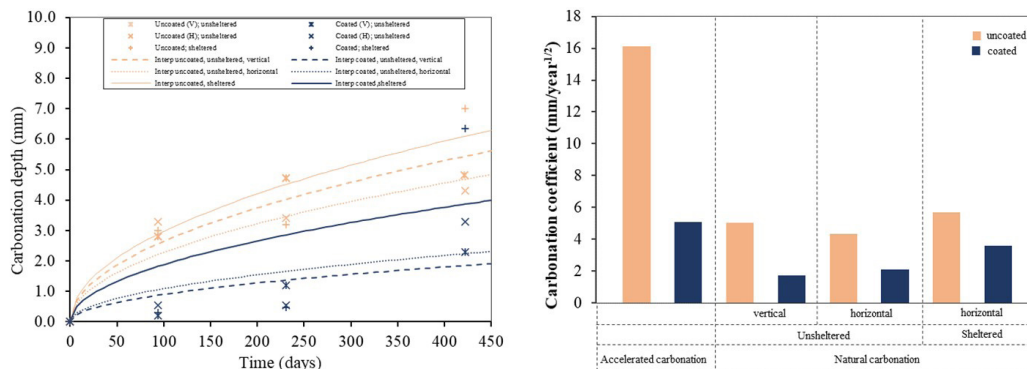
to UV light radiation).

For all cubic samples, carbonation depth was determined over time by splitting and phenolphthalein spraying on the freshly split surface (10 measures of the penetration of the carbonation in the penetrated surface were carried out in each test and the mean value was calculated). For the prismatic samples corrosion rates (by means of LPR technique) and corrosion potentials (with respect to activated titanium, Ti, and calomel reference electrode, SCE) of the embedded rebars as well as the electrical resistivity of the concrete were periodically measured.

## RESULTS AND DISCUSSION

### Carbonation depths in accelerated and natural conditions

Fig. 1 shows the measurement of carbonation depth in the coated and uncoated cubic samples during more than 420 days of exposure to natural carbonation and the determined carbonation coefficients for natural as well as accelerated carbonation (after more than 480 days of tests).



**Fig.1** - Penetration of carbonation in atmospheric conditions (left) and carbonation coefficients determined in accelerated and natural carbonation conditions (right) / Penetrazione della carbonatazione in condizioni atmosferiche (sinistra) e coefficienti di carbonatazione determinati in condizioni di carbonatazione naturale e accelerata (a destra).

In all exposures the carbonation depth and thus also the determined carbonation coefficient, was found to be significantly higher for uncoated samples (orange) in respect to the coated ones, with the hydrophobic pore liner (blue). Considering the first two measurements carried out after 94 and 231 days of atmospheric exposure (Fig. 1, left), average carbonation depth of 3 mm and 3.8 mm were determined for the uncoated specimens and 0.4 mm and 0.7 mm for the coated specimens, respectively. Slightly

differences were noted for the different orientations of the samples. In the first measures few differences between sheltered and unsheltered exposure were observed. In the latest measurement (after 422 days) a high increase in the penetration of the carbonation was detected in both samples, coated and uncoated, exposed to sheltered conditions. In unsheltered condition, the coated and uncoated samples showed a different behaviour. The carbonation depth has more than doubled in the coated sam-

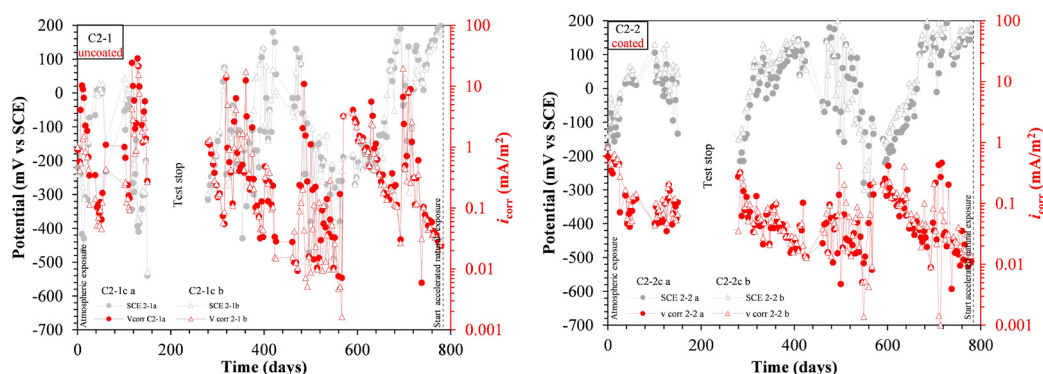
ples, from values of 0.5-1.2 mm measured after 231 days of exposure to 2.3-3.3 mm at 422 days, while the uncoated ones showed only a small increase, from 3.4-4.7 mm to 4.3-4.8 mm. This difference may be explained by the fact that this last test has been carried out in spring, thus the difference between sheltered and unsheltered conditions and coated and uncoated samples resulted higher than in the previous test carried out in autumn, after a summer period in which precipitations were nearly absent. The differences in carbonation depths between coated and uncoated samples in the last measures performed after 480 days of exposure were also observed in the samples submitted to accelerated carbonation. The carbonation depth in the coated samples increased from 0.7 mm (after 292 days) to 12 mm (after 483 days), while the depth measured in the uncoated specimen increased from 13 mm (292 days) to 19 mm (483 days). This strong increase in carbonation depth in the coated specimens after more than 1 year of test may be explained by the initial conservation of moister conditions in the superficial pores in the coated samples due to the gel form of the hydrophobic treatment. The evaporation of the water in the pores over time led to an increase in the penetration of the carbonation in respect to the initial measurements. However, in contradiction with some of the results reported in [6,8], the application of hydrophobic treatment decreased the penetration of the carbonation, both in natural and accelerated condition. The data measured over time on the samples in the different conditions were interpolated (Fig.

1, left) using the formula normally used to describe the penetration of the carbonation:  $s = K \cdot t^{1/2}$  [1]; where  $s$  is the carbonation depth (mm),  $t$  is the time (year) and  $K$  is the carbonation coefficient ( $\text{mm}/\text{year}^{1/2}$ ). Despite the last carbonation depth obtained for the coated samples resulted significantly higher than the previous measurements, in this paper the carbonation coefficient was determined interpolating all the data. Further measurements will be needed to analyse a possible change in the determination of this parameter. The estimated carbonation coefficients were reported in Fig. 1 (right). The uncoated samples showed values of  $K$  1.6-3 time higher in respect to coated ones in the different exposure condition. This beneficial effect of the coating seems to decrease over time, the next test at longer periods of exposure may provide further information on the long-time performance of the coating.

## CORROSION PROPAGATION

### Atmospheric exposure

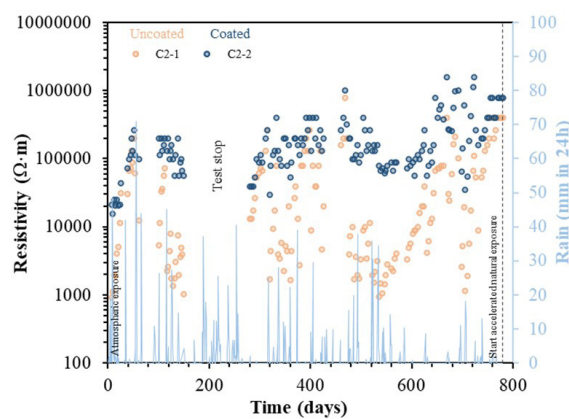
Fig. 2 shows the measurements of potentials in the uncoated (left) and coated (right) samples exposed to Milano atmosphere. The corrosion rates of the two rebars in the uncoated samples rised further after exposure in atmosphere (during the spring period), reaching values around  $30 \text{ mA}/\text{m}^2$  within the first 5 months of exposure (Fig. 2, left).



**Fig.2** - Corrosion rate and corrosion potential measured in uncoated samples (left) and coated samples (right) during the exposure to atmosphere (Milano) / Velocità di corrosione e potenziale di corrosione misurati nei campioni non rivestiti (sinistra) e rivestiti (destra) durante l'esposizione in atmosfera (Milano)

In the following months the corrosion rates as well as the potentials measured showed strong fluctuations due to the change in the weather conditions (Fig 3). The corrosion rate ranges from values of around 0.1 mA/m<sup>2</sup> to more than 10 mA/m<sup>2</sup> and the corrosion potential changes from measures below -400 mV vs SCE to values above 100 mV vs SCE. Rebars in the coated sample instead show a strong rise in potential from -120 mV vs SCE to +100 mV vs SCE in the first month of atmospheric exposure and the corrosion rate decreases to values < 0.1 mA/m<sup>2</sup> (Fig. 2, right). The electrochemical measures shows only some

slight fluctuation in the time; the corrosion rate remained always at values < 1 mA/m<sup>2</sup> (negligible propagation of corrosion) during all the period of atmospheric exposure. Fig.3 shows the measurement of concrete electrical resistivity in both samples over time (the cumulative value of the rainfalls in 24 hours is also reported). The resistivity of the uncoated sample (orange) was strongly affected by the weather conditions (mainly rainfalls, highlighted in light blue in the figure), as already noted for corrosion rate and potential.



**Fig.3** - Resistivity measurement in coated and uncoated samples during the exposure to Milano atmosphere; weather data obtained from [9] / Misure di resistività nei campioni con e senza rivestimento durante il periodo di esposizione all'atmosfera di Milano; dati meteo ottenuti da [9].

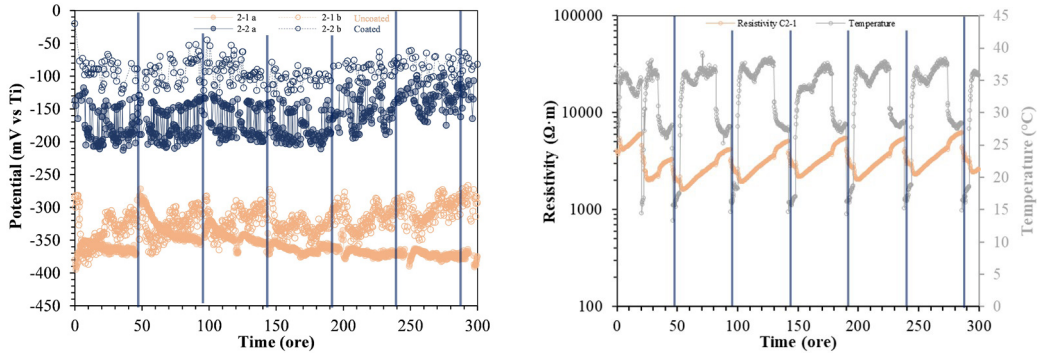
Higher precipitations led to a decrease in resistivity to values below 1000 Ω·m while in dry periods the resistivity rised to values higher than 100000 Ω·m. In the case of the coated sample (blue) the resistivity constantly remained around over 100000 Ω·m during the 2 years of exposure. The dry condition in the coated sample (high resistivity), thus prevented the propagation of corrosion (corrosion rate remained low and potential more positive) while the periodical drops in resistivity in the uncoated sample, and thus the higher availability of electrolyte in the concrete, allowed propagation of corrosion in the uncoated sample. The hydrophobic coating therefore proved to strongly prevent the ingress of water into the concrete and thus controls the propagation of reinforcement corrosion in carbonated concrete exposed to the atmosphere.

### Accelerated exposure

After 2 years of atmospheric exposure the prismatic sam-

ples were moved in a special chamber and subjected to 48 hours cycles 2 hours wetting by tap water (W), 4 hours drying by air ventilation (D) and subsequently 30 hours of exposed IR light and 12 hours to UV light (the indication reported in the standard ASTM G154-16 [10] was considered for the definition of this cycle). The exposure to these cycles was decided in order to accelerate the effect of the exposure in atmospheric condition.

Fig. 4, left shows, for a period of 300 hours, the continuous monitoring of the corrosion potentials of the rebars in the coated and uncoated sample during the exposure to the cycles. Fig.4, right shows the concrete resistivity monitored in the uncoated sample (C2-1) as well as the change in temperature on the concrete surface during the 48h cycles.



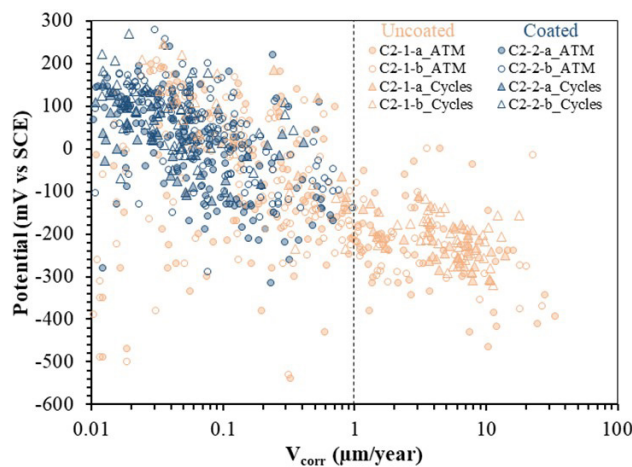
**Fig.4** - Monitoring of potential (left) and resistivity (right) during the exposure in the chamber (W/D/IR/UV) / Monitoraggio del potenziale e della resistività durante l'esposizione nella camera (W/D/IR/UV).

The potentials recorded in the uncoated samples (orange) are ranging between -400 and -280 mV vs. Ti for both rebars during the cycles. The wetting cycle (blue lines) led to a decrease in potential and the subsequent drying by ventilation, IR and UV light to following increase. Also, the concrete resistivity of the uncoated sample was found to be strongly influenced by the applied cycle (Fig. 4, right). The resistivities monitored in 300 hours were found to drop to 2000 Ω·m during each wetting cycle (in which 15°C was measured) and subsequently rise to about 5000 Ω·m during the dry period, in which temperature until 38°C were measured. The rebars in the coated sample (blue) showed a potential ranging between -70 and -210 mV vs. Ti and concrete resistivities higher than 35000 Ω·m were always measured.

Fig 5 reports the potentials and corrosion rates measured in the reinforced samples during the atmospheric and ac-

celerated exposure conditions. It may be observed, that all the measurements carried out for the rebars in the coated samples (blue) showed only a negligible propagation of the corrosion ( $V_{corr} < 1 \mu\text{m}/\text{year}$ ) in both, atmospheric (circles) and accelerated exposure (triangles). In the uncoated samples (orange), conversely, a negligible corrosion rate was detected only in atmospheric exposure during the period with low rainfalls, while during the wet periods and the exposure to the accelerated cycles (triangles) corrosion can propagate with a rate that reaches also values higher than 10  $\mu\text{m}/\text{year}$ .

Therefore, the coating proved to efficiently restrict the propagation of corrosion also in the more severe exposure to accelerated cycles and no degradation of the coating due to exposure to the cycles (in particular UV light or temperature change) was detected up to today.



**Fig.5** - Corrosion rate and corrosion potential measured in atmospheric and accelerated exposure condition / Velocità di corrosione e potenziale di corrosione misurati nelle condizioni di esposizione atmosferica e accelerate.

## CONCLUSIONS

The tests showed that, the hydrophobic pore lining treatment in gel form can efficiently increase the service life of reinforced concrete structures subjected to carbonation-induced corrosion. By application of the hydrophobic gel a reduction in the penetration of carbonation was observed, thus, a delay of corrosion initiation in reinforced concrete structures is to be expected. This effect decreases over time, however after 1.5 years of test a residual effect was still found. Additionally, the hydrophobic treatment proved to significantly decrease the propagation of

corrosion in carbonated concrete in atmospheric as well as accelerated exposure conditions. No degradation of the treatment (due to UV light or temperature or water) was observed after 2 years of exposure to Milano atmosphere and subsequent about 1 year to wet/air drying/IR/UV cycles (in which a maximum temperature of about 40°C was measured at the concrete surface).

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# Effetto di un rivestimento idrorepellente sulla corrosione da carbonatazione in strutture in calcestruzzo armato

La corrosione delle armature è la causa principale di degrado nelle strutture in calcestruzzo armato e comporta non solo problemi legati alla sicurezza delle persone, ma anche elevati costi per i necessari interventi di ripristino. La carbonatazione del calcestruzzo a contatto con le armature porta ad un consumo uniforme della sezione resistente delle armature, alla formazione di prodotti di corrosione espansivi e, di conseguenza, alla fessurazione e al distacco del copriferro. I trattamenti idrorepellenti possono essere un interessante metodo per controllare la propagazione della corrosione delle barre in calcestruzzo carbonatato e, quindi, per prolungare la vita di servizio delle strutture. In questo lavoro viene analizzato l'effetto di un rivestimento idrorepellente sull'innesco e sulla propagazione della corrosione da carbonatazione.

**PAROLE CHIAVE:** CORROSIONE, STRUTTURE IN CALCESTRUZZO ARMATO, CORROSIONE DA CARBONATAZIONE, RIVESTIMENTI SUPERFICIALI, TRATTAMENTO IDROREPELLENTE

**TORNA ALL'INDICE >**