



Carbonation of surface protected concrete



José B. Aguiar*, Cristela Júnior

Department of Civil Engineering, University of Minho, Campus of Azurém, Guimarães, Portugal

HIGHLIGHTS

- The carbonation of concretes with surface protection was evaluated.
- The concretes were protected with systems based in siloxane, acrylic and epoxy resins.
- The surface protected concretes presented lower carbonation diffusion coefficients than the non-protected concretes.
- The prescriptive methodology is not a guarantee to obtain the desired service lives of 50 or 100 years.
- The desired services lives were only obtained with the use of surface protection treatments.

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ABSTRACT

Concrete structures are exposed to carbonation that may cause rapid decay, shortening their service life and raising maintenance and repair costs. Carbonation lowers the alkalinity of the concrete depassivating the steel reinforcement. Two limit states can be identified with regard to service life. The first limit state ends when the steel is depassivated. The second limit state is based on cracking of the concrete cover due to oxides generated during corrosion. The service life includes a certain propagation period of corrosion during which the cross-sectional area of steel is progressively decreased, the bond between steel and concrete is reduced and the effective cross-sectional area of concrete is diminished due to spalling of the cover.

Surface treatment is commonly used to improve the resistance of concrete to carbonation. A barrier is formed retarding the carbonation reactions in the interior of the concrete. In this study surface protected concretes were compared with non-protected concretes. The used surface protected concretes presented generally lower carbonation diffusion coefficients than the non-protected concretes. The use of epoxy resin showed better protection than the use of acrylic and siloxane resins. The composition of the concretes is an important factor affecting the diffusion of carbonation. The influence of the water–cement ratio was very important. The carbonation diffusion coefficients increased with the water–cement ratio. The prescriptive methodology is not a guarantee to obtain the desired service lives of 50 or 100 years. The desired services lives were only obtained with the use of surface protection treatments.

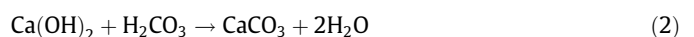
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1. Introduction

According to Eurocode EN 1992-1-1 [1] a durable structure shall meet the requirements of serviceability, strength and stability throughout its intended working life, without significant loss of utility or excessive maintenance. There is often a need for supplementary measures to protect concrete in aggressive environment. Surface treatment is commonly used to improve the resistance of such concrete against the penetration of aggressive substances, both in new and existing structures [2]. Various generations of surface protection materials have been developed to counteract the

aggressive actions of the environment against concrete. Between the most used we can find siloxane, acrylic and epoxy resins.

Natural concrete carbonation is a chemical reaction that involves the dissolution of atmospheric carbon dioxide in the pore water and the formation of a weak carbonic acid which dissociates and reacts with the calcium hydroxide resulting calcium carbonate and water [3]. The reactions are given in Eqs. (1) and (2), and a simplified graphic illustrating the reactions in Fig. 1.



However, in addition to these reactions the carbon dioxide also reacts with C–S–H in concrete to form additional calcium carbonate [4]. Carbonation starts at the concrete surface including the surfaces of any cracks throughout the life of the concrete [5]. After,

* Corresponding author. Fax: +351 253510217.

E-mail address: aguiar@civil.uminho.pt (J.B. Aguiar).

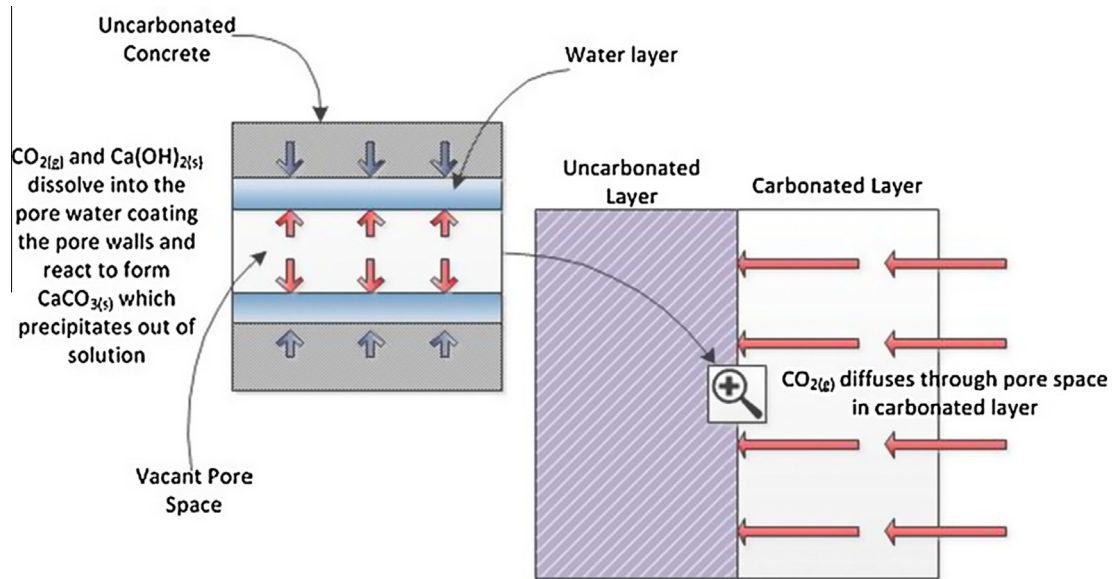


Fig. 1. Carbonation schematic [4].

carbonation penetrates inside of the concrete. This reaction lowers the alkalinity of the concrete depassivating the steel reinforcement [6].

Park [7] asserted that one-half of carbon dioxide in concrete reacts with calcium hydroxide while the other half reacts with C–S–H. This assertion was further supported by Glasser and Matschei [8] who showed that the reaction would occur in sequence, with calcium hydroxide first being consumed and then C–S–H reacting thereby densifying the microstructure.

Based on reference documents [9,10] the Portuguese standard NP EN 206-1 [11] for the design of concrete compositions includes two alternative specifications – prescriptive [12] and performance-based [13] – in view of environmental exposure.

The prescriptive methodology LNEC E464 [12] sets the limits of the concrete constituents (maximum w/c ratio, minimum cement dosage and cement type), the minimum compressive strength and the concrete cover thickness for a design working life of 50 years (target period) under the environmental exposures classes in issue. Eurocode 2 [1] defines and describes environmental exposure classes in view of the aggressive agent. For carbonation induced corrosion four classes are defined and described: XC1, XC2, XC3 and XC4 (Table 1).

The performance-based specification makes no restriction concerning constituents and dosage. The criterion is related to the modeling lifetime result (service life) based on testing results of accelerated carbonation on concrete samples of the designed concrete composition [6].

Two limit states can be identified with regard to service life (Fig. 2). This ends when the steel is depassivated. The limit state is based on cracking of the concrete cover due to oxides generated during corrosion. The service life includes a certain propagation

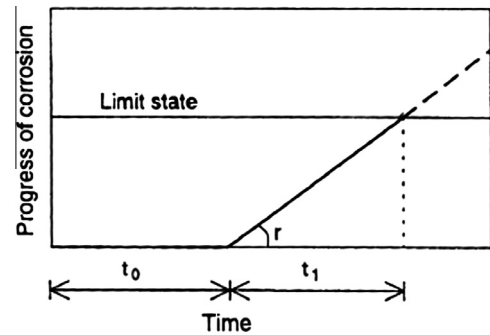


Fig. 2. Determination of service life with respect to corrosion of reinforcement [9].

period of corrosion during which the cross-sectional area of steel is progressively decreased, the bond between steel and concrete is reduced and the effective cross-sectional area of concrete is diminished due to spalling of the cover [9].

The initiation period concerning the penetration of carbon dioxide is based on the model of CEB [10] which the specification LNEC E465 [13] adopted considering the Portuguese environment. This model expresses the diffusivity of hardened concrete and it relates the concrete carbonation with time as follows:

$$x = \sqrt{\frac{2h}{R_{C65}}} \sqrt{k_0 k_1 k_2} \left(\frac{t_0}{t}\right)^n \tag{3}$$

where due to carbonation, steel depassivation starts when a depth x equals the concrete cover c of the reinforcement steel. R_{C65} ((kg/m³/

Table 1
Environmental exposure classes for carbonation induced corrosion [1].

Exposure class	Description	Informative examples where exposure classes may occur
XC1	Dry or permanently wet	Concrete inside buildings with low air humidity Concrete permanently submerged in water
XC2	Wet, rarely dry	Concrete surfaces subject to long-term water contact Many foundations
XC3	Moderate humidity	Concrete inside buildings with moderate or high air humidity External concrete sheltered from rain
XC4	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2

Table 2
Constant parameters k_1 and n for carbonation exposure classes [1].

Parameter	XC1	XC2	XC3	XC4
k_1	1.00	0.20	0.77	0.41
n	0	0.183	0.02	0.085

(m^2/year) defines the carbonation resistance obtained from the accelerated test with a relative humidity of 65% [14].

$$R_{C65} = \frac{2C_{\text{accel}}t_1}{X_1^2} = \frac{2C_{\text{accel}}}{k^2} \quad (4)$$

where X_1 is the carbonation depth (m), t_1 is the time (years), C_{accel} is the carbon dioxide concentration ($90 \times 10^{-3} \text{ kg/m}^3$), k is the carbonation coefficient ($\text{m}/\sqrt{\text{year}}$).

$\Delta C = 0.7 \times 10^{-3} \text{ kg/m}^3$ (difference of carbon dioxide concentration between the exterior and the carbonation front), $k_0 = 3$ is a constant value that accounts for the testing method and conditions [13,14], k_1 is the constant that accounts for the presence of relative humidity, k_2 is the constant that accounts for the curing influence: 1.0 for normalized cure and 0.25 for a 3 days period of curing, t_0 is the reference period = 1 year and n is the parameter that accounts for the wet/dry cycle influence in time [13]. Table 2 shows the values of parameters k_1 and n for all exposure classes.

The end of the initiation period to the depassivation due to carbonation and hence from Eq. (3) t becomes the initiation period t_i expressed as:

$$t_i = \left(\frac{R_{C65}c^2}{1.4 \times 10^{-3}k_0k_1k_2t_0^{2n}} \right)^{\frac{1}{1-2n}} \quad (5)$$

The performance-based specification [13] permits some flexibility in using water/binder ratios, dosage and types of cement different to those imposed by traditional prescriptive approach [12]. However the use of protection systems should be validated. This article presents results that include strength and carbonation of concretes protected and non-protected. Two concrete compositions were studied. One composition respects the prescriptive specification LNEC E464 [12]. The other composition does not respect this specification.

The surface protection materials for concrete can be classified into three groups: pore liner (makes the concrete water repellent), pore blocker (reacts with certain soluble concrete constituents and forms insoluble products) and coatings (form continuous film on concrete surface) [15]. This article study the carbonation of concretes protected with systems based in siloxane, acrylic and epoxy resins.

The starting product for most silicon-organic compounds is alkyl-trichloro-silane. By transformation of this silane with alcohol only, the corresponding alkyl-trialkoxo-silane is produced together with separation of hydrogen-chloride. The siloxane resins are obtained from the reaction of one silane with alcohol and water [16]. Acrylic resins are defined as a family of polymers resulting from the polymerization of derivatives of acrylic and methacrylic acids, such as butyl acrylate and methyl methacrylate, respectively [17,18].

Epoxy systems usually used as binders for coatings are two-component systems, one component containing the epoxy resin and the second the hardening agent. Most epoxy resins are synthesized by combining one molecule of bisphenol (derived from acetone and phenol) with two molecules of epichlorohydrin. This process forms the epoxy resin component, which contains both epoxide and hydroxyl functional groups. In polymerization, the resin molecules chemically react with a hardener to form the

Table 3
Chemical composition of the cement.

Chemical composition	CEM I 42.5R (%)
SiO ₂	19.64
Al ₂ O ₃	4.34
Fe ₂ O ₃	3.10
CaO	62.82
MgO	2.43
SO ₃	3.33
Cl ⁻	0.02
Loss on ignition	3.2
Insoluble residue	0.90

Table 4
Physical characteristics of the cement.

Physical characteristics	CEM I 42.5R
Density (kg/m^3)	3110
Blaine specific surface (m^2/kg)	3873
Fineness – 45 μm (%)	3.1
Water demand (%)	28.6

Table 5
Composition of the concretes.

Materials (kg/m^3)	Concrete 0.6 (C0.6)	Concrete 0.7 (C0.7)
Cement CEM I	280	280
Gravel 6–12	616	598
Sand 0–4	1284	1227
Water	171	199

polymer. The hardener commonly contains amine groups that react with the epoxide group [17,18].

2. Experimental program

2.1. Materials

Portland cement (CEM I 42.5) was used. Table 3 shows the chemical composition of the cement. Table 4 shows some physical characteristics of the selected cement. Two crushed granite were used as aggregates. One with a density of 2630 kg/m^3 , water absorption of 0.4%, fineness modulus of 5.94 and a maximum size of 12.00 mm. Another with a density of 2660 kg/m^3 , water absorption of 0.2%, fineness modulus of 3.95 and a maximum size of 4.00 mm.

Two types of concretes were used. The composition of the concretes is presented in Table 5. The two concretes had a cement content of 280 kg/m^3 . The results of the slump test were 10 mm for the concrete with water-cement ratio of 0.6 (C0.6) and 110 mm for the concrete with water-cement ratio of 0.7 (C0.7). The average compressive strength, at 28 days, for the concrete C0.6 was 35.0 N/mm^2 and for the concrete C0.7 was 27.0 N/mm^2 . The experimental campaign was designed in order to test unprotected and protected concrete specimens.

Surface protection products were selected to represent the following three generic types:

- Siloxane pore liner (S).
- Acrylic resin coating (A).
- Epoxy resin coating (E).

The three types were selected between the more used products for concrete protection. This study started with each generic type represented by two products from different producers. The selection was made as presented in a previous paper [19]. Table 6 presents some properties of the selected products. All materials were applied by brush on the lateral surface of the cylinders after curing for 28 days, following the recommendations of the producers. The surface protection materials hardened, under laboratory conditions, for 7 days before following the tests.

2.2. Carbonation test method

The carbonation tests followed the Portuguese specification LNEC E391 [14]. Testing samples were cylindrical with 100 mm diameter and 200 mm height. Before entering the carbonation chamber, samples were cured in water saturated environment until 14 days and after in the air at 50% RH and 20 °C till the age of 28 days. The following accelerated carbonation environment was 65% RH, 20 °C and 5% of

Table 6
Properties of the selected products.

Property	Siloxane resin in solvent	Acrylic resin aqueous based	Two component epoxy resin
Consistency	Liquid	Dense liquid	Dense liquid
Coverage rate (m ² /dm ³)	2.8	3.5	4.0
Density at 20 °C (kg/dm ³)	0.83	1.40	1.30
Brookfield viscosity at 20 °C (mPa s)	11	6000	1500
Surface drying time (min)	60	40	300
Interval between coats (h)	2	24	24

CO₂ air content. For each composition one sample was removed and had its carbonation depth analyzed at three different dates, 7, 14 and 28 days, after enter the carbonation chamber. Each sample was sliced in two halves and sprayed with phenolphthalein. The result of carbonation depth corresponds to the thickness with no change of color, while the remaining area (with change of color) indicates pH > 9. This method slightly underestimates the carbonation depth [20] since the reaction occurs for a pH < 10–11. This associated error was simply assumed and the procedure and corresponding analysis were nevertheless carried out [6].

3. Results and discussion

3.1. Carbonation tests

Fig. 3 presents the accelerated carbonation results of each concrete unprotected and protected. Although with some variation, it

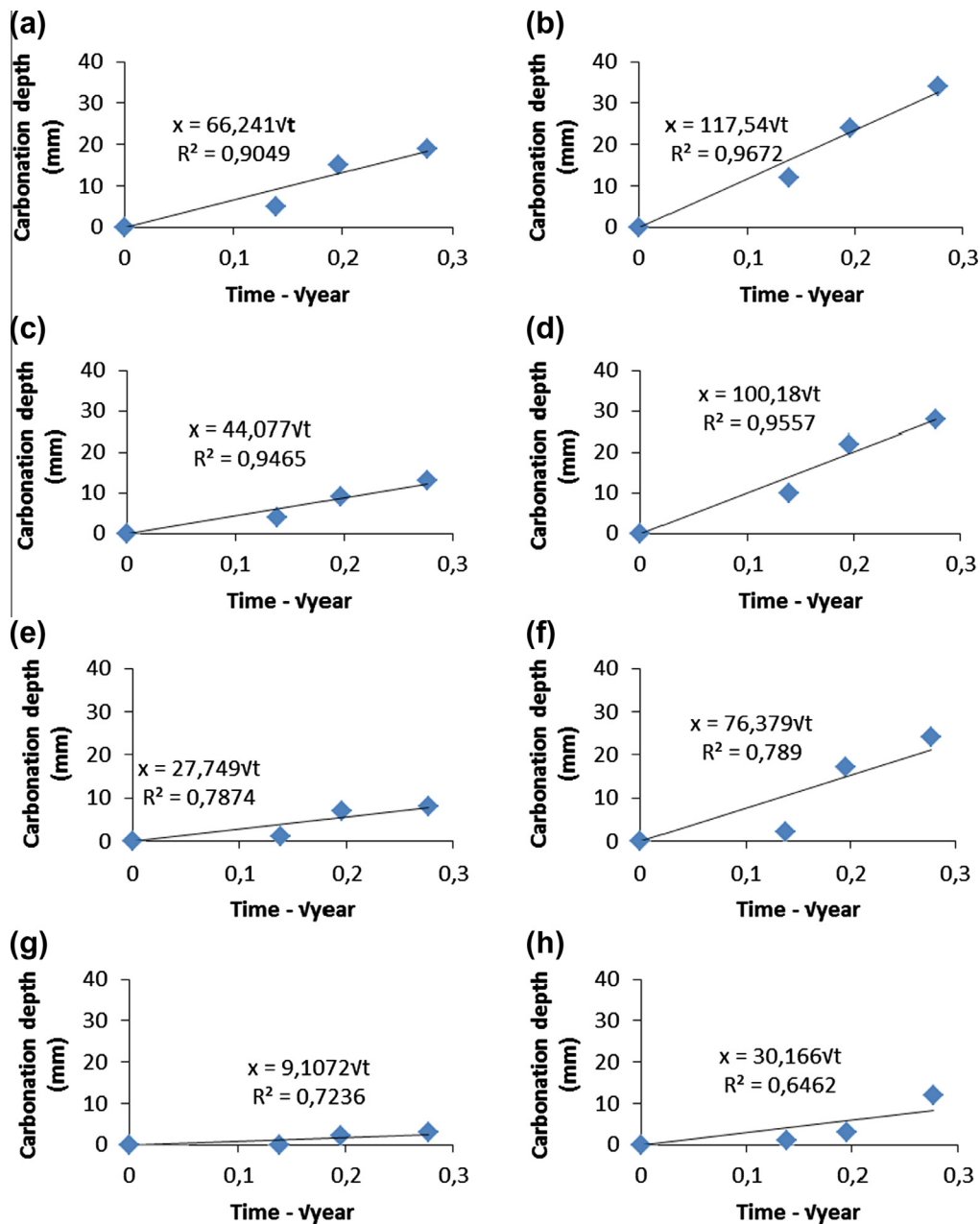


Fig. 3. Variation of accelerated carbonation depth with time (tests started at 28 days). (a) C0.6, (b) C0.7, (c) C0.6S, (d) C0.7S, (e) C0.6A, (f) C0.7A, (g) C0.6E, and (h) C0.7E.

Table 7
Results of carbonation diffusion k and carbonation resistance R_{c65} .

Concrete	Type of protection	K (mm/ $\sqrt{\text{year}}$)	R_{c65} ((kg/m ³)/(m ² /year))
C0.6	Unprotected	66	41
C0.7	Unprotected	118	13
C0.6S	Siloxane	44	93
C0.7S	Siloxane	100	18
C0.6A	Acrylic	28	230
C0.7A	Acrylic	76	31
C0.6E	Epoxy	9	2222
C0.7E	Epoxy	30	200

is considered that carbonation depth grows with the square root of time:

$$X = k\sqrt{t} \quad (6)$$

This way it is possible to obtain the carbonation coefficient k represented by the slope of each regression (Fig. 3 and Table 7). The correlation coefficients obtained are above 90% for the unprotected concretes and for concretes protected with the siloxane resin. For the concretes protected with acrylic and epoxy resin the correlation coefficients are situated always under 80%. This indicated that to take into account the presence of these resins, a regression different from linear may be considered to better represent the carbonation diffusion.

The carbonation diffusion coefficient increases with the water–cement ratio. Considering the tested unprotected concretes the carbonation diffusion increases about 79% comparing the concretes C0.6 with C0.7. Thomas et al. [21] also determined the variation of carbonation diffusion coefficient with the water–cement ratio. However between 0.6 and 0.7 they found an increase of about 40%. This increase of carbonation diffusion is due to the increase of the porosity with the water–cement ratio.

The protected concretes present usually lower carbonation diffusion coefficients than the unprotected concrete. However, the unprotected concrete C0.6 presents lower carbonation diffusion than the protected concretes C0.7S and C0.7A. This shows the importance of a low water–cement ratio in order to have low carbonation diffusion coefficient.

The siloxane resin reveals lower protection compared with the other protection systems. This is due to the nature of the siloxane resin that acts as pore liner, making the concrete water repellent. On the contrary the acrylic and epoxy resins act as coatings, forming continuous film on concrete surfaces. Epoxy resin presents better protection than acrylic resin confirming the results of Park [7]. The carbonation diffusion coefficient decreased about 65% comparing concretes protected with acrylic resin (C0.6A and C0.7A) with concretes protected with epoxy resin (C0.6E and C0.7E)

3.2. Service life analysis

Marques et al. [6] present two methods for the modeling of the initiation period: the partial safety factor method (semi-probabilistic) and the probabilistic method [13]. The results obtained with these two methods were similar [6]. So, in this study only the first method will be used.

The estimation of the service life period using the partial safety factor method has been carried out considering the exposure class XC4 for the target periods t_g of 50 and 100 years with a cover $c_{\text{min,dur}}$ of respectively 40 and 50 mm. The analysis was based on an established assumption [13,22] that the performance limit is expressed as reliability index $\beta \geq 1.5$ or probability of failure $P_f \leq 7\%$.

The propagation period corresponds to the beginning of corrosion of steel reinforcement within the concrete. This causes the

loss of section of steel bars which results into loss of strength of the steel reinforcement itself. Additionally, there is an increase of volume of the corrosion product around steel bars which leads to internal stresses against the surrounding concrete and consequent loss of bond between concrete and steel [23].

The specification LNEC E465 [13] specifies different minimum propagation periods t_p for each exposure class and different minimum required target periods t_g (Table 8). The design service life, t_L , is calculated as:

$$t_L = \frac{t_i}{\gamma} + t_p \quad (7)$$

where t_i is the initiation period obtained from Eq. (5), γ is the safety factor associated to the reliability class (Table 9), and t_p is the propagation period given in Table 8.

Table 10 shows the results of design service life of RC structures included in exposure class XC4 using a safety factor of $\gamma = 2.3$ (Eq. (7) and Table 9). About the unprotected concretes, the required service life of 50 years is only reached with the concrete C0.6 and for dry region. The required service life of 100 years is not reached with both concretes C0.6 and C0.7. This is an unexpected result because at least the concrete C0.6 should reach the required service lives because its composition respect all the exigencies of the specification LNEC E464 [12]. Marques et al. [6] used concrete also with CEM I but with lower water–cement ratio (0.55) and with higher cement content (330 and 360 kg/m³). The design service life found by Marques et al. [6] was about 180 years and 350 years for required service lives of 50 years and 100 years, respectively.

The design service life increases with the surface protection. The higher service life was obtained with the epoxy resin protection (C0.6E and C0.7E). About protected concretes the lower service life was obtained with siloxane resin (C0.6S and C0.7S). This is due to the type of barrier formed by the different protection systems. The siloxane resin acts as pore liner and both acrylic and epoxy resins act as continuous coating. The acrylic and epoxy resins also present high viscosity.

The concrete with water–cement ratio of 0.6 reached the desired service lives with all the protection systems tested (C0.6S, C0.6A and C0.6E). About the other concrete, with water–cement ratio of 0.7, the desired service life was only obtained with the epoxy resin protection (C0.7E). Design values of service life higher than 200 years are difficult to be accepted as realistic.

The used method did not take into account the degradation of the protection systems. Under real circumstances, organic coatings degrade naturally as a result of heat, moisture, ultraviolet radiation, etc. [7]. In order to guarantee the high values obtained with

Table 8
Minimum propagation periods from corrosion onset until cracking [13].

Exposure class	$t_g = 50$ years	$t_g = 100$ years
	t_p Estimated (years)	t_p Estimated (years)
XC1	>100	>100
XC2	10	20
XC3	45	90
XC4	15 – dry region	20 – dry region
	5 – wet region	10 – wet region

Table 9
Safety factor γ values for each reliability class [13].

Reliability class	Safety factor value
RC1	2.0
RC2	2.3
RC3	2.8

Table 10

Design service life: partial safety factor method – class XC4.

Concrete	R_{CS} ((kg/m ³)/(m ² /year))	$t_g = 50$ years $c_{min,dur} = 40$ mm t_L (years)	$t_g = 100$ years $c_{min,dur} = 50$ mm t_L (years)	Region
C0.6	41	40	70	Humid
		50	80	Dry
C0.7	13	14	25	Humid
		24	35	Dry
C0.6S	93	99	170	Humid
		109	180	Dry
C0.7S	18	18	32	Humid
		28	42	Dry
C0.6A	230	284	488	Humid
		294	498	Dry
C0.7A	31	30	53	Humid
		40	63	Dry
C0.6E	2222	>500	>500	Humid
		>500	>500	Dry
C0.7E	200	241	414	Humid
		251	424	Dry

the protection resins it will be important their reapplication after periods of about 10–15 years.

4. Conclusion

The used surface protected concretes presented generally lower carbonation diffusion coefficients than the non-protected concretes. This is due to the barrier effect introduced by the use of such surface protections. The use of epoxy resin showed better protection than the use of acrylic and siloxane resins. The composition of the concretes is an important factor affecting the diffusion of carbonation. The influence of the water–cement ratio was very important. The carbonation diffusion coefficients increased with the water–cement ratio. This is due to the increase of the porosity of the concrete. The prescriptive methodology is not a guarantee to obtain the desired service lives of 50 or 100 years. The desired service lives were only obtained with the use of surface protection treatments.

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