Civil Engineering
Engenharia Civil

Surface treatment systems for concrete in marine environment: Effect of concrete cover thickness

http://dx.doi.org/10.1590/0370-44672014690092

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Abstract

There are some ways to extend the service life of a reinforced concrete structure. This paper focuses on the extension of the service life by treating the surface of reinforced concrete, specifically on the effect of the concrete cover thickness on the surface treatment system efficacy. Thus, chloride migration tests were performed and diffusion chloride coefficients were calculated. The service life of each case (treated or non-treated concrete) was estimated using these data and Fick's second law of diffusion. Results indicated that the thicker the concrete cover is, the greater the efficacy of the concrete surface treatment system will be. The dissemination of this information is important, since it is almost intuitive to think that the effect of a surface treatment system depends only on itself and this study shows the opposite.

Keywords: chloride, concrete, durability, surface protection, service life.

1. Introduction

When a structure has its construction completed, the layman thinks its materialization costs have ceased. However, under the action of usage, it will need to undergo maintenance to ensure the proper performance of its functions.

Under standard conditions, the reinforcing steel is physically protected by a barrier consisting of the concrete cover. This barrier limits the ingress of substances that can start the corrosion process and limits the access of water and oxygen. Having a good quality concrete, with high density and high electrical resistivity, it will be less susceptible to ionic movements, and therefore, the corrosion process will slow down.

However, it is not only the concrete cover variable that interferes in the depassivation time and kinetics of reinforcement corrosion. Some studies such as Guimarães *et al.* (2003) and Meira *et al.* (2007) show the influence of the distance of the structure in relation to the sea, showing that the attack intensity is severely reduced when distance from the coastline increases. Medeiros *et al.* (2013) studied an in situ reinforced concrete structure showing that the higher the concrete is, the lower the chloride contamination degree will be and showed the influence of the wetting and drying cycles which increase the speed of chloride contamination. These are important aspects, indicating that service-life models and building standards should consider these effects. However, many research works are needed to make possible the improvement and production of more realistic and accurate service life models.

In this context, surface treatment is an alternative to increase the service life of reinforced concrete structures. The aim of this work is to study the increase in service life caused by the protection of concrete surfaces exposed to marine environments. More specifically, to study the influence of concrete cover thickness on the potential protective systems of surface treatments for concrete in an environment contaminated with chloride ions.

2. Experimental program

2.1 Concrete substrate

The concrete of the substrate was produced with a Brazilian Portland cement designated CPII E-32, which is equivalent to ASTM C 595 (Slag-modified Portland cement). This cement has blast furnace slag addition and is one of the most widely used cements in the state of São Paulo, Brazil.

The mix proportioning of the concrete was 1:1.80:2.70 and water/cement ratio equals 0.52, which corresponds to a compressive strength of 32 MPa (28 days, in saturated condition). The maximum size of coarse aggregate is 19 mm.

Curing occurred at 23^{o}C and 100% RH environment during 91 days, used to obtain a high degree of hydration. This was chosen because migration tests involve the exposure of the surfaces to moisture and this could cause additional hydration in untreated concrete but not in concrete with treated surface.

2.2 Surface Protection Systems

Five protection systems were used, all are commercial products specified for surface treatment of reinforced concrete structures exposed to chloride ions environments. Table 1 presents a summary of the studied surface protection products. The choice of these protection systems aims to compare some products of the three groups of surface protection systems: Pore liners (make the concrete water-repellent), pore blockers (react with some of the soluble concrete constituents and form insoluble products) and coatings (form continuous film on the concrete surface).

Group	Treatment system	Identification	Description manufature
Pore liners	Single	Water repellent	Silane/siloxane – dispersed in water
Pore blocker	Single	Sodium silicate	Product based on sodium silicate marketed for protection and waterproofing of concrete
Coating	Single	Acrylic	Varnish Acrylic – dispersed in solvent
	Single	Polyurethane	Varnish polyurethane (Bicomponent)
Double system	Double	Water repellent + Acrylic	(silane/siloxane – dispersed in water) + (Varnish acrylic – dispersed in base solvent)

Table 1
Description of the
systems included in the study.

The consumption of material indicated by the manufacturers was respected in the implementation of all protection systems used in this work.

2.3 Chloride migration test (non-steady state condition)

The migration tests were conducted similarly to the ASTM C 1202/12 procedure, but with some modifications. The differences are the voltage applied, of 30 V (instead of 60 V), the 30-hour testing time (instead of 6 hours) and the measurement of the chloride penetration depth (instead of total charge passed).

After curing time, each cylindrical specimen (100 mm in diameter and 200 mm in length) was cut into two 50-mm-wide slices from the central nucleus of the original specimen. Although most researchers adopt the use of a single central slice for the migration test, in this study they were drawn from two central slices based on a previous work (Medeiros et al. 2009 and Medeiros *et al.* 2012a), which statistically proved that it is totally possible to use up to three 50-mm thick slices in a migration test without compromising the results. Six slices were used to represent each case studied.

After the drying procedure (7 days in laboratory environment – 25 ^{o}C and R.U. 70±4%), the protection materials were applied on only one circular surface of the specimens. Afterwards, the specimens were vacuum-saturated during 24 hours. This procedure consisted in conditioning specimens in vacuum desiccators and applying a vacuum pressure of 1 mmHg (133 MPa) during 3 hours. Then, the desiccator was filled with de-aerated water until all specimens were immersed, and the vacuum pressure was maintained for one additional hour. Afterwards, the vacuum pump was turned off, and the specimens were maintained immersed during 20 hours.

Seven days after the application of the surface treatment, the 50-mm-thick specimen was placed between two acrylic cells, each cell with 280 cm^3 of solution volume. One cell was filled with 0.3 N NaOH aqueous solution and the other with 3.0% NaCl aqueous solution. The cells were connected to a 30 V power source during 30 hours, in which the electrode immersed in NaOH aqueous solution was the anode and the electrode immersed in 3.0% NaCl aqueous solution was the cathode.

After 30 hours of the migration test, the concrete slices were fractured in the direction of the chloride flux and an aqueous solution of $AgNO_3$ 0.1 M was sprayed on the recently fractured surface. This procedure causes the formation of two well-defined regions (one white, one brown). The white region is formed due to AgCl precipitation, and, therefore, represents the region containing chlorides. The brown region corresponds to the region free of chlorides. Importantly, the white region corresponds to the site with free chloride (water soluble chloride), and the measurement refers to the front of free chloride penetration excluding the combined chloride (Meck and Sirivivatnanon 2003).

Luping and Nilsson (1992) established a mathematical model to determine the chloride diffusion coefficient in non-steady-state conditions. The chloride diffusion coefficient calculation according to these authors is performed using Equation 1.

$$D = \frac{RT}{zFE}\,\frac{x_d - a x_d^b}{t} \qquad (1)$$

Where: R = gas constant (8.31 J / molK); T = temperature (298 K); z = is the ion valence (for chloride = -1); F = Faraday constant (96.5 J / Vmol); E = electric field (-600 V / m); x_d = chloride penetration depth (m); t = test time (s), a and b = constants. When E = -600 V / m and T = 298 K, a = 1.061 and b = 0.589. This method is based on chloride migration in non-steady-state conditions (according to Fick's law). According to Luping and Nilsson (1992), with this procedure, the test time is a few hours for conventional concrete and about 2 days for high performance concrete. In the experiment used here, the testing time was 30 hours. Andrade *et al.* (2000) compared different methods for determining the diffusion coefficient in unsteady-state conditions and concluded that this procedure is the one with better reproducibility of results.

3. Results and discussion

Table 2 presents chloride diffusion coefficient data measured with the procedure formerly described for the reference concrete (without treatment) and for concrete studied with different surface treatments.

Table 2
Chloride diffusion
coefficient measured in each case.

Identification	Chloride diffusion Coefficient (cm^2/s)
Reference (untreated)	3.52E-08
Water repellent	3.06E-08
Acrylic	2.75E-08
Polyurethane	1.02E-08
Water repellent + Acrylic	1.17E-08
Sodium silicate	1.99E-08

Using the chloride diffusion coefficient values determined by the method proposed by Luping and Nilsson (1992) and applying the second Fick's law (non-steady-state conditions), it is possible to construct Figure 1, which relates the concrete cover with the service life in respect to chloride attack.

In this way, equations 3 and 4, developed by the second Fick's law (Equation 2), were used.

$$\frac{C_{cl} - C_o}{C_s - C_o} = 1 - erf\left(\frac{e_{cl}}{2\sqrt{Def_{cl}\,t}}\right) \qquad (2)$$

Where: C_{Cl} = chloride content at depth e_{Cl}, at time t (%); C_s = chloride content in the surface of the concrete, admitted as constant (%); C_0 = initial chloride content in concrete; Def_{Cl} = effective chloride diffusion coefficient (cm^2/s); t = time considered (s); e_{Cl} = depth reached of chloride content equals C_{Cl} (cm).

Considering z a given variable and isolating e_{Cl}, Equation 3 is obtained.

$$z = \frac{e_{cl}}{2\sqrt{Def_{cl}\, t}} \Rightarrow e_{cl} = 2z\sqrt{Def_{cl}\, t} \qquad (3)$$

Including z in Equation 2 and isolating erf(z), Equation 4 arrives.

$$erf\,(z) = 1 - \frac{C_{cl} - C_o}{C_s - C_o} \qquad (4)$$

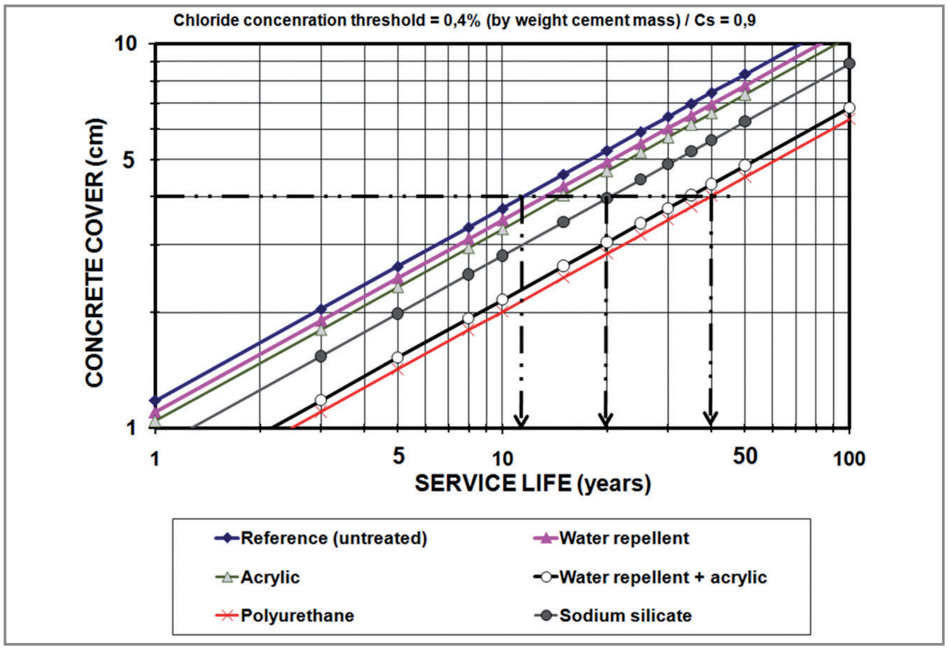

Figure 1
Estimated service life (years) for untreated concrete and with the various surface protections systems of the study (diffusion coefficient by Luping; Nilsson method, 1992).

In the construction of Figure 1, $C_0 = 0$ was considered because there is no chloride in the concrete at the time of molding the specimens.

Fixing a value for C_S and considering C_{Cl} equal to the critical chloride content limit for corrosion initiation in reinforcement, the Gauss error function [erf (z)] is found. Using tables that relate erf (z) with z, the value of z is obtained. By replacing the value of z and the chloride diffusion coefficient (obtained by the test) in Equation 3, an equation relating the depth at which the threshold value (for depassivation reinforcement) is reached with the time needed for the steel corrosion depassivation to be obtained. This was the reason for preparing Figure 1.

To construct this plot, a value equal to 0.9% of CS extracted from Helene (1993) was used, which specifies this reference value for concretes with compressive strength between 20 and 30 MPa, water/cement from 0.48 to 0.68 subjected to salt spray. This is the range at which the concrete substrate of this work fits.

Moreover, it should be noted that, in the present study, the term service life means the time required for the chloride content, on the surface of the reinforcement, to reach 0.4% (in respect to cement mass), which corresponds to the period called corrosion initiation. The value of 0.4% was chosen as it was the most internationally accepted as the chloride threshold for corrosion initiation, although this issue still needs to be well researched in order to reach a consensus.

It is important to highlight that the approach adopted in this paper for the solution of the second Fick's law, according to Andrade and Dal Molin (2003), is called "Error Function solution" which implies the following simplifications:

- It is assumed that the concrete material is homogeneous and isotropic;
- The only active transport mechanism is diffusion;
- It is assumed that no interactions occur between the chlorides and the components of the concrete at the time of penetration;
- The medium is considered to be infinite;
- Both the chloride diffusion coefficient and the chloride content at surface are constant over time;
- Chloride diffusion coefficient is completely independent of surface concentration.

It is known that there is a mistake in this methodology, since C_S tends to increase and chloride diffusion coefficient decreases over time. C_S increases due to the accumulation of chlorides in the concrete surface during the exposure time and the diffusion coefficient decreases due to changes in the concrete microstructure.

As indicated by the arrows in Figure 1, for a given structure with a concrete cover thickness equal to 4 cm, the treatments resulted in increases in service life of 15%, 28%, 244%, 77% and 200% for water repellent, acrylic, polyurethane, sodium silicate and double system, respectively.

Figure 2 has an overview of the increase in service life (in years) as a function of the concrete cover. It is worth to note that the larger the concrete cover is, the larger the gain in years provided by the protection, i.e., the difference between the reference series and the treated concrete is more evident.

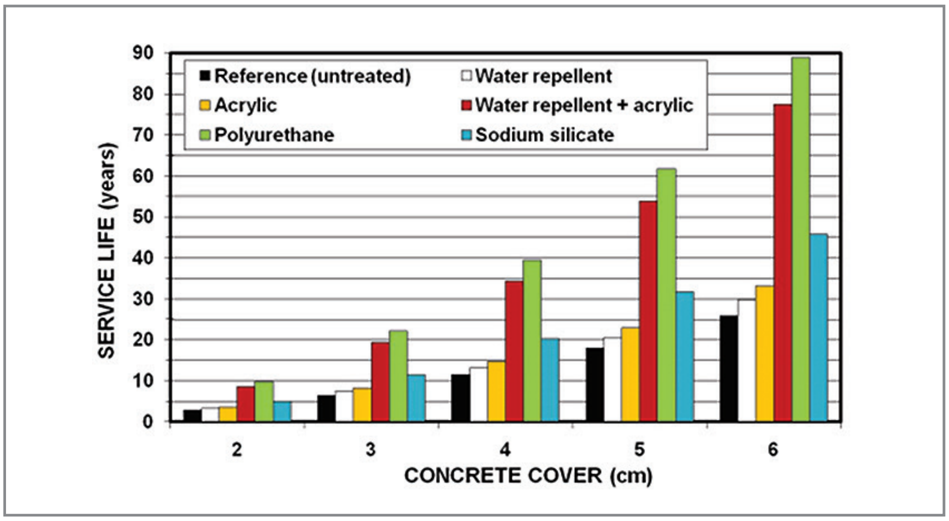

Figure 2
Concrete cover X service life for concrete treated with water repellent - C_s = 0.9% (diffusion coefficient by the Luping and Nilsson method, 1992).

Figure 3 helps to understand this fact, showing relation between the number of years of service life attained with each protection system and the designed concrete coverage or the existing concrete cover, in the case of an old reinforced concrete structure to be protected.

A very useful way to think in terms of surface protection was proposed in Medeiros and Helene (2009) and Medeiros *et al.* (2012b), in which protection is converted to the equivalent concrete cover, which consists of how many inches of concrete cover thickness equal to one coat of a given protection system. The equivalent concrete covers for water repellent, acrylic, water repellent + acrylic, polyurethane and sodium silicate are 0.3 cm, 0.5 cm, 2.9 cm, 3.4 cm, and 1.3 cm, respectively.

It is important to emphasize that the service life predictions presented in this work are only valid under the conditions listed below:

- The reinforced concrete structure is at the beginning of its service life (starting from the initiation period);
- The fastest degradation agent is chloride attack;
- No accidental external factors have affected the properties of the concrete cover.

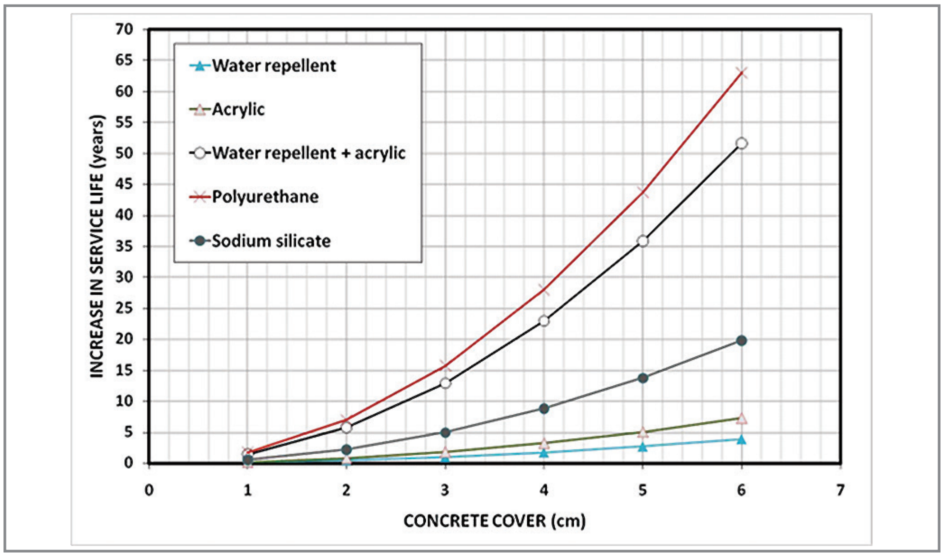

Figure 3
Concrete cover X increase in service life for treated and untreated concrete - C_s = 0.9% (diffusion coefficient by the Luping and Nilsson method, 1992).

It is important to emphasize that there is a consideration that was made in this work and can be considered as a point of method failure. It is the fact that the concrete+surface protection was not considered as a two-layer system and thus has two different diffusion properties.

However, it is difficult to consider the thickness of each layer existing in cases where hydrophobic agents and silicates have been applied, since these treatments do not form a layer. These products penetrate the pores of the concrete and act by chemical reaction. Thus, it becomes difficult to treat the situation as two layers.

In the case of acrylic and polyurethane would be possible to measure the layer using a meter-thick layer of paint, but it was thought better not to give different interpretation procedures for the treatments being tested in this work. For this reason, all cases in this study were considered as a single layer with a single chloride diffusion coefficient.

4. Conclusions

The results presented here show that the effect of raising the service life of a surface protection for concrete exposed to marine environment is highly influenced by the thickness of the existing concrete cover. This means that the thicker the concrete cover of the reinforcement is, the higher the increase of service life offered by a particular protection system will be. This information is important for professionals involved in designs of new reinforced concrete structures as well as in repairs of existing structures, helping decision-making in the specification of materials for surface protection.

The dissemination of this information is important, since it is almost intuitive to think that the effect of a surface treatment system depends only on itself and this study shows the opposite. There is an influence of the concrete cover of the existing reinforced concrete structure in the performance of the surface treatment system.

This study indicates a method for testing and analyzing reinforced concrete subjected to chloride environment based on a simple chloride migration test and the use of Fick's diffusion law. This may be an important tool for analyzing this type of material to define the specification of surface protection systems.

This paper shows the high capacity for increasing service life presented by surface protection systems; they can double or even triple the structure service life. However, it is important to emphasize that this increase is inherent to a regular maintenance program and schedule. This is essential due to the fact that the durability of protection systems is extremely lower than the durability of the concrete structure, and periodical maintenance is thus required to ensure their efficiency in protecting the concrete substrate over time.

5. Acknowledgements

The authors thank the University of São Paulo (POLI-USP), the Federal University of Parana (UFPR), the Institute for Technological Research of São Paulo (IPT) and FAPESP (The State of São Paulo Research Foundation) for making this study possible by financially supporting it.

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Received: 30 May 2014 - Accepted: 15 June 2016.