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Numerical Study on Chloride Ingress in Cement-Based Coating Systems and Service Life Assessment

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Abstract

Chloride induced corrosion is a critical issue for reinforced concrete structures. Cement-based coatings can be used to protect the concrete structures with unsatisfactory quality against the chloride ingress. To evaluate the effectiveness of the coatings to extend the service life of the coated concrete structures, evolution of chloride profile in the coated concrete structures should be determined. This paper investigated the mechanism of chloride ingress into coated concrete structures (i.e., coating made of cement paste + concrete substrate). A numerical tool is proposed for calculating the chloride profiles in the coated concrete structures. Parameter study is carried out to investigate the influences of several factors on the chloride ingress, viz. the w/c ratio of the coating, the thickness of the coating, and early or late application of the coating. Preliminary cost analysis of coating materials is carried out. The results show that the effectiveness of the coatings increases with the coating thickness and with a drastic increase of material cost; the effectiveness of the coatings increases with the decrease of the w/c ratio and with a moderate increase of material cost. In order to extend the service life of the substrate, a coating with a low w/c ratio is recommended, while the coating thickness should be designed depending on the requirements. Moreover, the exposure history of the substrate before application of the coating also has an influence on the effectiveness of the coating. In order to protect an existing concrete structure exposed to the chloride environment against rapid chloride ingress, it is preferable to apply a coating as early as possible, since the effectiveness of the coating is reduced by a late application.

Keywords: cement-based coating; concrete substrate; simulation; chloride ingress; service life assessment.

Introduction

Concrete has a good performance in compression, but is weak in tension. Reinforcement is commonly used to take up tensile forces in concrete structures. The reinforcement in concrete structures is normally passivated due to high alkalinity in concrete. Depassivation of the reinforcement will take place when the chloride content at reinforcement reaches a critical value (Tuutti 1982). The critical chloride content has been identified to be one of the most decisive parameter for predicting the service life of concrete structures (Gulikers 2006). In practice, the initial scatter in the quality of concrete is unavoidable, possibly resulting from improper design, poor execution, or deterioration due to stresses during the service life of concrete structures (e.g. external load, stress induced by temperature, drying shrinkage or ingress of chemical substances, etc.). Areas of concrete with poor quality may become a path for aggressive substances to penetrate into the concrete, like chloride ions, resulting in premature deterioration due to corrosion of the reinforcement. To protect the reinforced concrete structures against chloride ingress, both polymer coatings and cement-based coatings have been applied (Swamy and Tanikawa 1993; Saricimen et al. 1996; Al-Dulaijan et al. 2000; Moon et al. 2007; Bolzoni et al. 2011; Diamanti et al. 2013; Almusallam et al. 2002). Cement-based coatings are preferably used when there is a requirement of color similarity to the concrete structure or a requirement of preservation of the alkaline nature of the concrete pore solution (Al-Dulaijan et al. 2000). Note that this study focused on existing concrete structures with initial scatter in quality, possibly resulting from improper design, poor execution, or deterioration due to stresses. Cement-based coatings are applied on the existing concrete structures to extend their service life. Increasing concrete cover thickness in the design phase of the concrete structures is another solution for reaching the designed service life while out of the scope of this study.

In order to give guidance to the design of the coating material, the effectiveness of the coating material to extend the service life of the coated concrete structures needs to be evaluated. For the evaluation of the effectiveness of the coating material, chloride ingress in to the coated concrete structures should be investigated. There are two forms of chlorides in coating material and concrete substrate, namely free chloride and bound chloride. The free chlorides exist in pore solution, while the bound chlorides are either chemically or physically bound to hydration products (Tang and Nilsson 1993). Chloride transport in hardened concrete has been comprehensively studied with or without consideration of chloride binding (Mangat and Molloy 1994; Thomas and Bamforth 1999; Xi and Bazant 1999; Nielsen and Geiker 2003; Tang and Gulikers 2007). According to Martin-Perez et al. (2000), the chloride binding behavior has a substantial influence on chloride transport in cement-based materials. It suggests that the chloride binding behavior should be considered in the simulation of chloride ingress.

Only few numerical studies are known to simulate chloride transport in concrete overlay systems (Zhang et al. 1998; Song et al. 2009). Zhang et al. (1998) and Song et al. (2009) simulated chloride ingress into concrete repair systems. The evolution of chloride profile in the repair system was determined. The results showed that the repair material reduced chloride ingress into concrete substrate, and the service life of the reinforced concrete substrate was extended (Zhang et al. 1998; Song et al. 2009). However, the hydration process of overlay material and the chloride binding behavior of both the overlay material and the concrete substrate are not considered in their studies. Note that in a concrete overlay system, hydration of overlay material takes place after application of the overlay material. The microstructure of the overlay material changes with the progress of the hydration process, resulting in the changes of chloride diffusivity and chloride binding capacity. Therefore, the hydration process of the overlay material and the evolution of the chloride diffusivity and the chloride binding capacity have to be considered for simulating chloride transport in cement-based overlay systems. It should be pointed out that, the hydration process in the substrates also needs to be considered, if the coatings are applied on young concrete substrates in which the hydration process has not completed.

This study numerically investigates chloride ingress into cement-based coating systems (Fig. 1). Fresh coating material is applied either on a young concrete substrate (7-day old) or on an old concrete substrate (e.g., 5, 10 or 20-year old). The chloride ingress into cement-based coating systems is simulated, taking into account the hydration process of the coating and the young concrete substrate. Fig. 2 shows the flow chart for the simulation of chloride transport in a hydrating cementitious coating system (e.g., a coating is applied on a young concrete substrate). Parameter study is performed to investigate the influences of several factors on chloride ingress into concrete structures, viz. the water to cement ratio of the coating, the thickness of the coating, and early or late application of the coating. With the parameter study, the influence of each factor on the chloride ingress into the coated substrates is evaluated. Based on the simulated chloride profiles, the service life of the coated concrete structures is predicted with a critical free chloride content at the surface of steel reinforcement. This study gives insights into the design and the application of cement-based coatings for the protection of reinforced concrete structures.

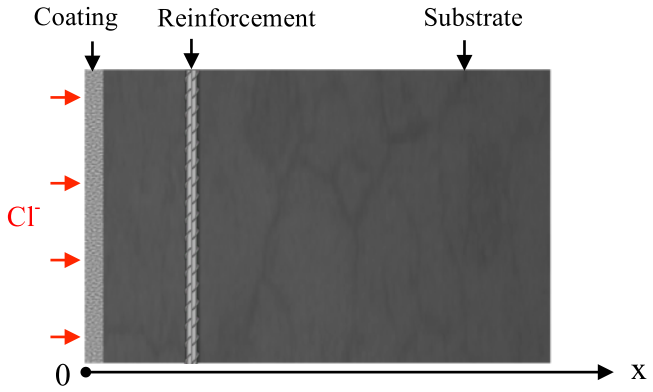


Fig. 1 Schematic of chloride ingress into a cement-based coating system. The coating is applied on a concrete substrate.

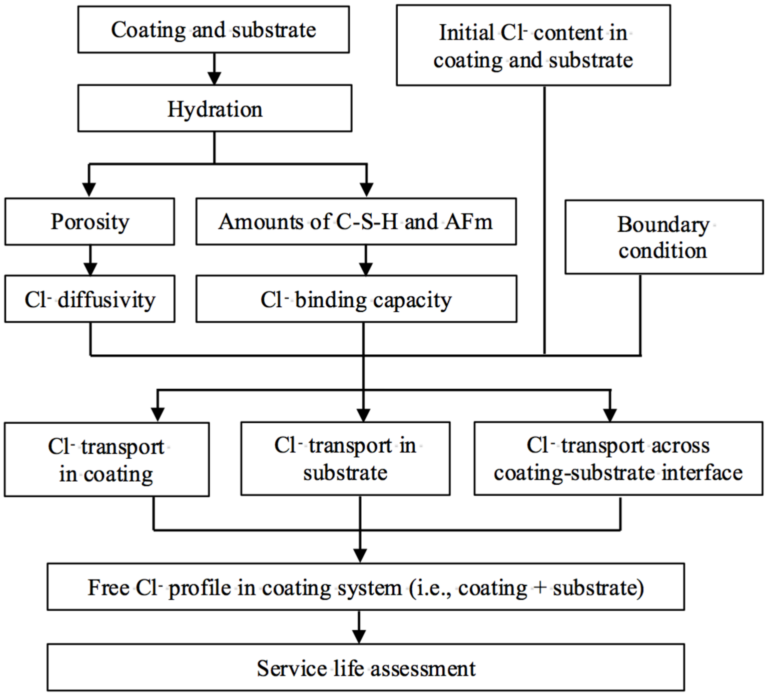


Fig. 2 Flowchart for simulation of chloride transport in a hydrating cementitious coating system.

Mechanisms of chloride ingress in hydrating coating systems

Chloride transport in hydrating cement-based materials

The total chloride content in cementitious materials consists of free chloride and bound chloride. The total chloride content is commonly expressed relative to the weight of cement, mortar or concrete (Mangat and Limbachiya 1999; Bentz et al. 2013). Insofar chloride penetration is determined by diffusion, Fick's 2nd law is commonly used to describe the diffusion process of free chloride ions.

$$\frac{\partial C_c}{\partial t} = div(D_{Cl} \cdot grad\ C_c) \tag{1}$$

where C_c is the free chloride content in concrete (kg/m^3 of cement-based material), t is the time (s). D_{Cl} is the chloride diffusivity (m^2/s), quantification of D_{Cl} for coating and substrate will be given in Eq. (11) and Eq. (12), respectively.

In fact, the chloride diffusion is driven by the gradient of concentration of free chloride in the pore solution of the material. The concentration of free chloride C_f (in mole of Cl$^-$ per liter of pore solution) needs to be calculated from the free chloride content C_c (Xi and Bazant 1999):

$$C_f = \frac{C_c}{M_{Cl} \cdot \phi} \tag{2}$$

where M_{Cl} is the molar mass of chloride (g/mol), ϕ is the total porosity of the material.

By substituting Eq. (2) in Eq. (1), a new form of Eq. (1) reads:

$$\frac{\partial \phi \cdot C_f}{\partial t} = div\left[D_{Cl} \cdot grad\left(\phi \cdot C_f\right)\right] \tag{3}$$

To account for the chloride binding effect, the term $\partial C_f / \partial C_t$ is introduced:

$$\frac{\partial C_f}{\partial C_t} = \frac{\partial C_f}{\partial C_f + \partial C_b} \tag{4}$$

where C_t is the total chloride content in the material and consists of the free chloride C_f and the bound chloride C_b. The unit of C_t is usually expressed as kg/m^3 of the material. In numerical calculations, the unit of C_t is preferably transformed into mole of Cl$^-$ per liter of pore solution.

$\partial C_f / \partial C_t$ can be determined based on the chloride binding isotherm which describes the relationship between the amount of bound chloride C_b and total chloride C_t (Midgley and Illston 1984). By introducing $\partial C_f / \partial C_t$ into Eq. (3), a new form of Eq. (3) reads:

$$\frac{\partial \phi \cdot C_f}{\partial t} = \frac{\partial C_f}{\partial C_t} \cdot div\left[D_{Cl} \cdot grad\left(\phi \cdot C_f\right)\right] \tag{5}$$

After rearrangement, Eq. (5) becomes:

$$\phi \cdot \frac{\partial C_t}{\partial C_f} \cdot \frac{\partial C_f}{\partial t} = div\left(\phi \cdot D_{Cl} \cdot grad\ C_f\right) - C_f \cdot \frac{\partial \phi}{\partial t} \cdot \frac{\partial C_t}{\partial C_f} \tag{6}$$

The initial concentration of free chloride $C_f(t = 0, x)$ in the materials and the surface (i.e. exposed surface) chloride concentration $C_f(t, x = 0)$ (see Fig. 1) are described as:

$$C_f(t = 0, x) = C_o \tag{7}$$
$$C_f(t, x = 0) = C_s \tag{8}$$

where C_o and C_s are the values of the initial concentration of free chloride in the materials and the surface chloride concentration, respectively.

Chloride transport across coating-substrate interface

When simulating chloride transport in a coating system, attention has to be paid to the coating-substrate interface (Fig. 3). The flux of free chloride across the interface is determined by several parameters: viz. the gradient of free chloride in the coating system, the chloride diffusivity and the porosities of the coating material and the substrate.

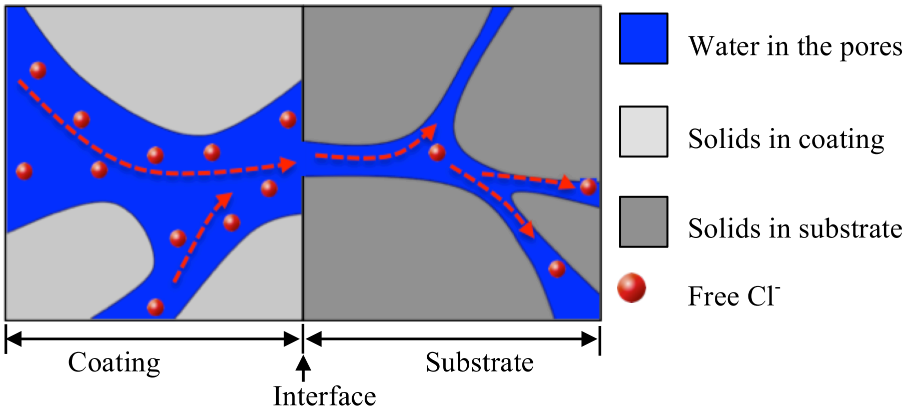


Fig. 3 Schematic illustration of chloride diffusion across the coating-substrate interface.

In order to conserve the mass of chloride in the coating system, two criteria should be fulfilled. One criterion is the continuity in concentration of free chloride at the coating-substrate interface (Eq. (9)).

$$C_{f_{c0}} = C_{f_{s0}} \tag{9}$$

where $C_{f_{c0}}$ and $C_{f_{s0}}$ are concentration of free chlorides at the interface.

Another criterion is the continuity in the flux of chloride at the coating-substrate interface. The flux of concentration of free chloride across the coating-substrate interface J_{Cl-int} is described by Fick's 1st Law (Eq. (10)):

$$J_{Cl-int} = -\phi_c \cdot D_{Cl-c} \cdot grad\ C_{f_c} = -\phi_s \cdot D_{Cl-s} \cdot grad\ C_{f_s} \tag{10}$$

where ϕ_c and ϕ_s are the porosities of the coating and the substrate, respectively. D_{Cl-c} and D_{Cl-s} are the chloride diffusivity of the coating and the substrate, respectively. C_{f_c} and C_{f_s} are the free chloride concentrations in the coating and the substrate at the interface, respectively.

Eq. (6) - Eq. (10) govern the chloride transport in coating systems. By specifying a boundary condition (i.e. a surface chloride concentration in Eq. (8)), the evolution of the free chloride profile in the coating system can be simulated.

Quantification of material properties for the simulation

To run the simulation, the porosity, the chloride diffusivity and the chloride binding isotherm of the coating and the substrate should be quantified.

Total porosity of coating and substrate

Pores in cement-based materials are usually classified into capillary pores (pore size $>$ 10 nm) and gel pores (pore size $\leq$ 10 nm) (Mindess et al. 1981). Capillary pores are the residual unfilled space between cement particles, while gel pores are entirely contained within C-S-H (Jennings and Tennis 1994). To determine the capillary porosity and the gel porosity of the coating and the substrate, the degree of hydration should be known. In this study, the development of the degree of hydration α of the coating and the substrate is determined by HYMOSTRUC3D (Van Breugel 1991; Koenders 1997). The HYMOSTRUC3D model enables the prediction of hydration curves as a function of the particle size distribution and chemical composition of the cement, the w/c ratio of cement paste and the actual reaction temperature. In HYMOSTRUC3D model, only water in capillary pores is considered freely available for cement hydration. During the hydration process, the water in capillary pores is gradually consumed. Note that the original version of HYMOSTRUC3D deals with cement hydration under sealed condition. This study uses a modified version of HYMOSTRUC3D, which simulates cement hydration under saturated condition by specifying 100% water saturation level in capillary pores. Based on the degree of hydration α, the capillary porosity ϕ_{cap} of the cement paste is calculated (Van Breugel 1991). The gel porosity ϕ_{gel} is also calculated from the degree of hydration following the methodology proposed in the literature (Jennings et al. 2008; Tennis and Jennings 2000; Taylor 1987), taking into account the amounts of high-density and low-density C-S-H gels. The total porosity of the cement paste is calculated with $\phi = \phi_{cap} + \phi_{gel}$. When calculating the porosity of the concrete substrate, pores in the interface transition zone are not considered in the calculation, but should be considered in future study for a more precise determination of the total porosity ϕ.

Chloride diffusivity of coating and substrate

The chloride diffusivity depends on the microstructure and the water saturation of cement-based materials (Nielsen and Geiker 2003). For a hydrating cement-based material cured under saturated condition, the chloride diffusivity is time-dependent (Tang and Nilsson 1992). Gaboczi and Bentz (1992) proposed an equation (Eq. (11)) to predict the chloride diffusivity $D_{Cl-c}(t)$ of ordinary Portland cement paste:

$$\frac{D_{Cl-c}(t)}{D_0} = 0.001 + 0.07 \cdot \phi_{cap}(t)^2 + H\left[\phi_{cap}(t) - \phi_c\right] \cdot 1.8 \cdot \left[\phi_{cap}(t) - \phi_c(t)\right]^2 \qquad (11)$$

where D_0 (m^2/s) is the chloride diffusivity in free water, $\phi_{cap}(t)$ is the capillary porosity at time t. ϕ_c is the percolation threshold of capillary pores (taken as 0.18 (Garboczi and Bentz 1992)), $H(x)$ is a Heaviside function, with $H(x) = 0$ for $x \leq 0$, and 1 for $x > 0$.

Eq. (11) is based on the capillary porosity ϕ_{cap} of cement-based material. Above the percolation threshold ϕ_c, the capillary pores dominate the diffusion process. When the capillary pores become disconnected, chloride ions have to diffuse through gel pores, indicating a lower chloride diffusivity. Eq. (11) is used to calculate chloride diffusivity of coating material investigated in this study.

The diffusivity of concrete substrate depends on the cement matrix, the aggregates and the interfacial transition zone (ITZ) (Caré 2003; Carrara and De Lorenzis 2017). For simplification, only the cement matrix and the aggregates are considered for determining the chloride diffusivity of the concrete, despite that the ITZ also plays a role (the diffusivity can be scaled up by a factor of 2 due to the presence of the ITZ, depending on the volume fraction of the ITZ (Caré 2003)).

The diffusivity of concrete substrate $D_{Cl-s}(t)$ can be determined based on a composite model developed by Christensen (2012):

$$D_{Cl-s}(t) = D_{Cl-c}(t) \cdot \left\{1 + \frac{g_{agg}}{(1 - g_{agg})/3 + D_{Cl-c}(t)/[D_{agg} - D_{Cl-c}(t)]}\right\} \tag{12}$$

where g_{agg} is the volume fraction of the aggregates. D_{agg} is the diffusivity of aggregate. When the type of aggregate is unknown, the value of D_{agg} can be simply taken as 1×10^{-12} cm^2/s (Xi and Bazant 1999).

Chloride binding isotherm

The binding isotherm highly depends on the chemical composition of the materials. Hirao et .al (2005) investigated chloride binding isotherms of C-S-H and AFm hydrates. They found that the chloride binding isotherm of AFm follows a Freundlich-type adsorption (Hirao et al. 2005):

$$C_{b-AFm} = 0.86 \cdot C_f{}^{0.58} \tag{13}$$

where C_{b-AFm} is the bound chloride, in moles of chloride per mole of AFm.

The chloride binding isotherm of C-S-H follows a Langmuir-type adsorption (Hirao et al. 2005):

$$C_{b-CSH} = 0.61 \cdot \frac{2.65 \cdot C_f}{1 + 2.65 \cdot C_f} \tag{14}$$

where C_{b-CSH} is the bound chloride in mili-moles of chloride per gram of C-S-H, and C_f is free chloride in moles of free chloride per liter of pore solution.

In order to combine them and incorporate them in Eq. (6), it is necessary to use the same unit for free and bound concentrations. For this reason, bound chloride $\mathrm{C'}_{\mathrm{b-AFm}}$ and $\mathrm{C'}_{\mathrm{b-CSH}}$ are introduced, with the unit in moles of chloride per gram of hydration products:

$$C'_{b-AFm} = 0.0014 \cdot C_f^{\ 0.58} \tag{15}$$

$$C'_{b-CSH} = 0.0017 \cdot C_f / \left(1 + 2.65 \cdot C_f\right) \tag{16}$$

The mass of monosulphate M_{AFm}, the mass of C-S-H gel M_{CSH}, and the total porosity ϕ are needed for the calculation of the total amount of bound chloride C_b (Eq. (17)). The unit of M_{AFm} and M_{CSH} is in kilograms of hydrates per cubic meter of cement-based material.

The C-S-H gel is the hydration product of C_3S and C_2S. C_3A and C_4AF are two sources for the formation of AFm. Given the total degree of hydration, the amounts of C-S-H ($\mathrm{M_{CSH}}$) and AFm ($\mathrm{M_{AFm}}$) can be determined (Jennings et al. 2008; Taylor 1987). Total amount of bound chloride C_b, with the unit in mol/L, is written as:

$$C_b = \left(M_{CSH} \cdot C'_{b-CSH} + M_{AFm} \cdot C'_{b-AFm}\right) / \phi \tag{17}$$

The term $\partial C_f / \partial C_t$ in Eq. (6) can be calculated:

$$\frac{\partial C_f}{\partial C_t} = \frac{\partial C_f}{\partial C_f + \partial C_b} = \left[1 + \frac{0.0017 \cdot M_{CSH}}{\phi \cdot \left(1 + 2.65 \cdot C_f\right)^2} + \frac{M_{AFm}}{\phi} \cdot \left(0.0008 \cdot C_f^{\ -0.42}\right)\right]^{-1} \tag{18}$$

Validation of the model for simulating chloride ingress in cement-based coating system

The experimentally obtained chloride profile in a two-layer sample by Yu et al. (1993) is used to validate the model proposed in this paper. In the experiments, two cement paste specimens (ordinary Portland cement was used, w/c = 0.5) were prepared. In one specimen, 2% chloride (as $NaCl$) by weight of cement was added during mixing. In another specimen, no chloride was added. After 90-day sealed curing at 25 ± 2 °C, the two cement paste samples (49 mm in diameter and 65 mm in length) were cemented together by a thin layer of fresh cement slurry (w/c = 0.5) (Fig. 4). The cemented samples were sealed. Chloride diffusion and chloride binding start to take place in the cement pastes. After 225 days of sealing, the concentration of free chloride profile in the samples was measured by extracting the pore solution (Fig. 5). The best-fit chloride diffusivity of the 90-day old cement paste was calculated to be $D_{Cl} = 3.93 \times 10^{-12}$ (m^2/s), and considered as constant throughout the test (Yu et al. 1993).

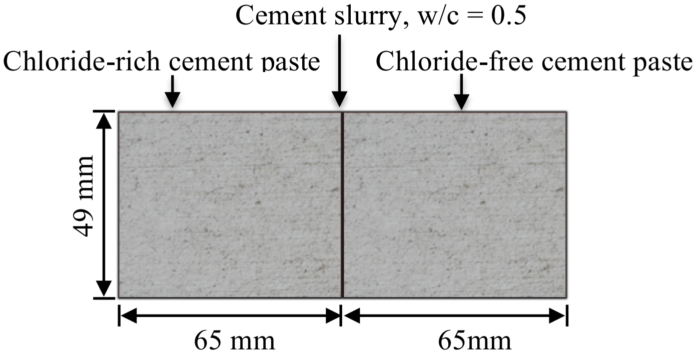


Fig. 4 Schematic of two cement pastes that are cemented by a cement slurry. This is a setup of experiments in Yu et al. (1993).

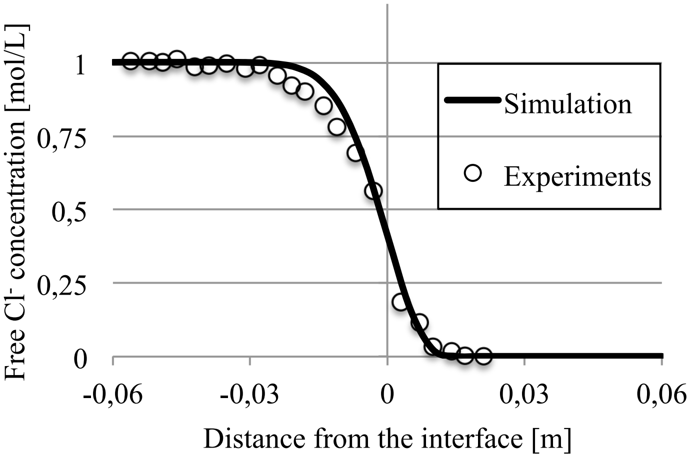


Fig. 5 Comparison of free chloride profiles in two cemented specimens between experiments and simulation. Two 90-day-old specimens are cemented together by a fresh cement slurry. Left side, chloride-rich samples, right side, chloride-free sample (Fig. 4). After 225 days, free choride profile is determined (Experimental data from Yu et al. 1993).

Chloride transport in the two-layer cement paste sample is simulated using the model proposed in this paper. Two cement pastes (w/c = 0.5) made of ordinary Portland cement are bound together and cured under sealed condition for 90 days. The same chloride diffusivity $D_{Cl} = 3.93\times10^{-12}\ (m^2/s)$ obtained in Yu's experiments (Yu et al. 1993) is adopted. According to simulations with HYMOSTRUC3D, the degree of hydration of the samples is about 80% after 90-day sealed curing at 20 ℃. The porosities (i.e., capillary porosity and gel porosity) of the samples can be determined based on degree of hydration. In partially saturated cement paste, chloride transport can only take place in water-filled pores. For sealed samples, the porosity ϕ in Eq. (6) refers to the water-filled porosity ϕ_w (Eq. (19), which consists of the water-filled capillary porosity ϕ_{cap-w} and the gel porosity ϕ_{gel}.

$$\phi_w = \phi_{cap-w} + \phi_{gel} \tag{19}$$

According to Van Breugel (1991), the water-filled capillary porosity ϕ_{cap-w} can be determined by:

$$\phi_{cap-w} = \frac{V_{w-0} - 0.4 \cdot \alpha \cdot m_{cem}/\rho_w}{V_{cp}} \tag{20}$$

where V_{w-0} is the volume of mixing water per m^3 of cement paste, m_{cem} is the volumetric content of cement and calculated by $m_{cem} = \rho_{cem} \cdot \rho_w / [\rho_w + \rho_{cem} \cdot (w/c)]$, α is degree of hydration, ρ_w is density of water and V_{cp} is unit volume of cement paste.

The simulated free chloride profile in the specimens at 225 days after the two specimens are cemented together is presented together with experimental data shown in Fig. 5. The simulated profile agrees well with the experimental data. The comparison of the experimental and simulation results in this figure indicates that the simulation tool proposed in this chapter is able to appropriately consider the chloride diffusion in two-layer cementitious system with consideration of chloride binding. Therefore, the use of the simulation tool for simulating chloride transport in cementitious coating systems (i.e., cement paste as a coating + concrete substrate) is considered justified.

Simulation of chloride transport in coating systems and service life prediction of the reinforced concrete substrate

This section presents numerical simulations of chloride transport in hydrating cement-based coating systems. Based on the simulated free chloride profiles, the service life of the reinforced concrete substrate is predicted. The effectiveness of the coatings to extend the service life of the substrates is evaluated. One-dimensional (1D) simulations are conducted.

Materials of coating systems (coating and substrate)

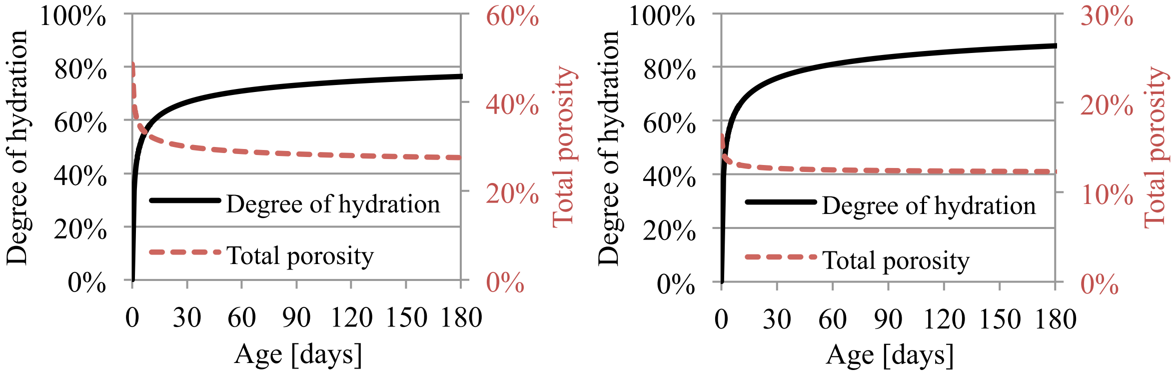
The coatings are made of cement pastes. Ordinary Portland cement (OPC) is used (mineral composition: C_3S : C_2S : C_3A : C_4AF = 53.5% : 21% : 7.5% : 10.7%). Cement chemists' notation is used throughout this study, with C = CaO, S = SiO_2, A = Al2O_3, F = Fe_2O_3 and H = H_2O. Different w/c ratios (0.3, 0.4 and 0.5) are considered for the coatings. The same cement (OPC) is used in concrete substrate. The volume fraction of aggregates in the substrate is 70%. The materials used in the coating systems are summarized in Table 1.

Table 1 Materials used in the coating systems.

Component	Description	Cement content	w/c	Thickness (mm)
Coating	Cement paste		0.3, 0.4 or 0.5	3, 6 and 10
Substrate	Concrete*	350 kg/m^3	0.48	150

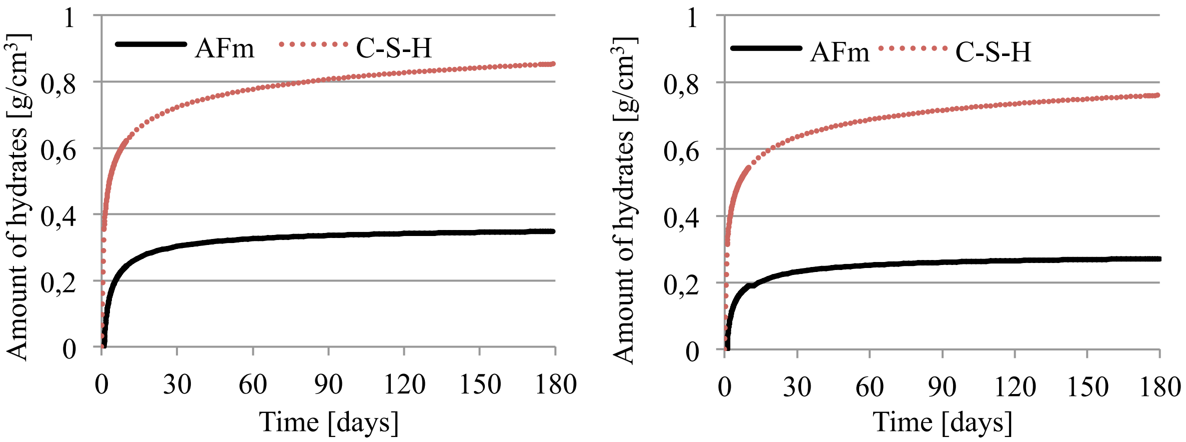
* The contents of sand and gravel in concrete substrate are 734 kg/m^3 and 1184 kg/m^3, respectively.

The hydration processes of the coatings and the substrate under saturated condition are simulated by HYMOSTRUC3D. Fig. 6 shows the evolution of the degree of hydration and the total porosity of the coating (w/c = 0.3) and the substrate (w/c = 0.48). Time "0" in Fig. 6 refers to the time when the raw materials of the coating or the substrate are mixed. The hydration process of the coating and the substrate takes place quickly in the first 7 days. After 7 days, the rate of hydration becomes slow. The amounts of C-S-H and AFm in the coating and the substrate are presented in Fig. 7, and used for determining the term $\partial C_f/\partial C_t$ accounting for chloride binding. Fig. 8 shows the calculated chloride diffusivities of the coating and the substrate (see Eq. 11 and Eq. 12). At the same curing age, the coating has a lower chloride diffusivity than the substrate, due to the lower w/c ratio (w/c = 0.3) of the coating than that of the substrate (w/c = 0.48). The term accounting for chloride binding of the coating and the substrate, $\partial C_f/\partial C_t$, is calculated with Eq. (18) and presented in Fig. 9. The ratio of free chloride to total chloride, $\partial C_f/\partial C_t$, decreases with increasing degree of hydration, indicating an increasing chloride binding capacity. At the same degree of hydration, the substrate (w/c = 0.48) has a higher ratio of free chloride to total chloride (i.e. a higher value of $\partial C_f/\partial C_t$ or lower chloride binding capacity) than the coating (w/c = 0.3). This can be explained by the fact that the substrate has a higher water-to-cement ratio than the coating. The higher water-to-cement ratio of the substrate leads to lower amounts of C-S-H and AFm (C-S-H and AFm are two hydrates that bind chlorides).



(a) Coating (w/c = 0.3) (b) Substrate (w/c = 0.48)

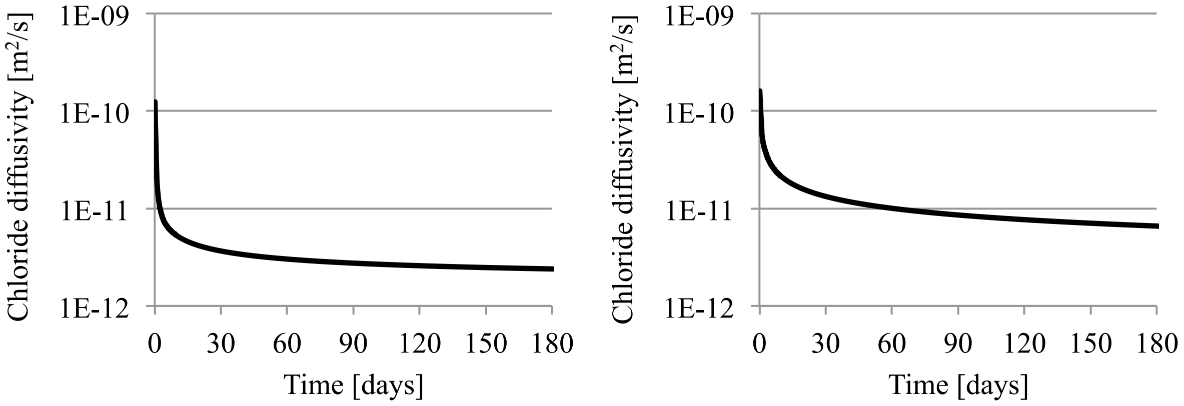
Fig. 6 Degree of hydration and total porosity of the (a) coating (w/c = 0.3) and (b) substrate (w/c = 0.48).



(a) Coating (w/c = 0.3)

(b) Substrate (w/c = 0.48)

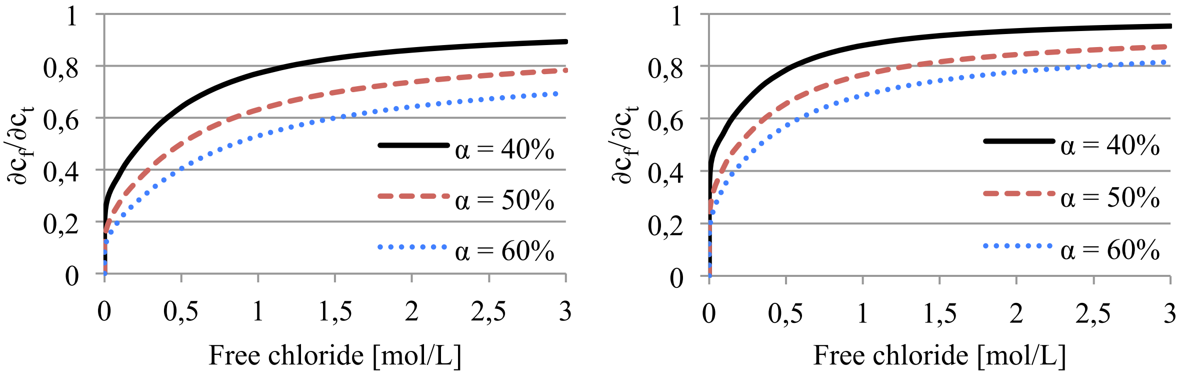
Fig. 7 Evolution of degree of hydration and amounts of hydrates (in g per cm^3 of cement paste) of the (a) coating (w/c = 0.3) and (b) substrate (w/c = 0.48). Saturated condition is considered for the hydration of both coating and substate.



(a) Coating (w/c = 0.3)

(b) Substrate (w/c = 0.48)

Fig. 8 Chloride diffusivity D_{cl} of the (a) coating (w/c = 0.3) and (b) substrate (w/c = 0.48).



(a) Coating (w/c = 0.3) (b) Substrate (w/c = 0.48)

Fig. 9 Ratio of free chloride to total chloride, $\partial C_f / \partial C_t$, accounting for chloride binding capacity of the (a) coating (w/c = 0.3) and (b) substrate (w/c = 0.48).

Exposure scenario for the coating systems and parameters to be evaluated

Exposure scenario for the coating systems

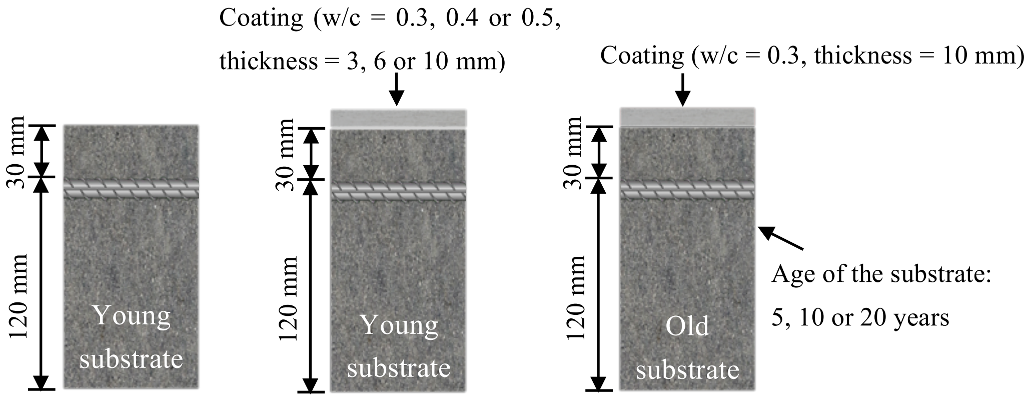
The coating is applied on a concrete substrate (Fig. 1). The surface with the coating is exposed to chloride environment; the other surface of the substrate is sealed. Steel reinforcement is placed at a 30 mm from the exposed surface. In the simulation, the coating system is considered saturated.

Parameters to be evaluated

Chloride transport in the uncoated substrate (Fig. 10a) is taken as a reference for evaluating the effectiveness of the coatings. Coatings with different w/c ratios and different thicknesses (Fig. 10b) are applied on young substrates (7 days after casting). In practice, coatings may also be applied on old substrates. To simulate this scenario, coatings are applied on old concrete substrates that have been exposed to chloride environment for a period of time (Fig. 10c). The parameters to be evaluated are listed in Table 2.

Table 2 Parameters considered in the numerical simulation.

Parameters	Description
w/c of coating material	Coating material (thickness = 10 mm) with a w/c of 0.3, 0.4 or 0.5
Coating thickness	Coating material (w/c = 0.3) with a thickness of 3, 6 or 10 mm
Early/late application of coating	The coating materials (w/c = 0.3, thickness = 10 mm) are applied on young substrates, or on old substrates that have been exposed to chloride environment for 5, 10 or 20 years



(a) substrate (b) coating on young substrate (c) coating on old substrate

Fig. 10 Schematic illustration of (a) substrate, (b) coating on young substrate, and (c) coating on old substrate systems. The coatings with different w/c ratios and thicknesses are applied on young/old substrates.

Abbreviations and descriptions of the coating systems are presented in Table 3. The coating systems are classified based on the w/c ratio of the coating, the thickness of the coating, the time of coating failure, early or late application of the coating and the depth of the surface crack in the substrate.

Table 3 Abbreviated designations of the concrete substrate and the coating systems (the coatings and the substrates are saturated).

Designation	Coating thickness and w/c ratio[a]	Substrate[b]
Sub		Young Substrate
C10(wc0.5)-S	10 mm (w/c = 0.3)	Young Substrate
C10(wc0.4)-S	10 mm (w/c = 0.4)	Young Substrate
C10(wc0.3)-S	10 mm (w/c = 0.5)	Young Substrate
C06(wc0.3)-S	6 mm (w/c = 0.3)	Young Substrate
C03(wc0.3)-S	3 mm (w/c = 0.3)	Young Substrate
C10(wc0.3)-S05y	10 mm (w/c = 0.3)	5-year old Substrate
C10(wc0.3)-S10y	10 mm (w/c = 0.3)	10-year old Substrate
C10(wc0.3)-S20y	10 mm (w/c = 0.3)	20-year old Substrate

[a] After application of the coating, 0.5 days moist curing is applied to the coating system, followed by an exposure to the chloride environment.

[b] A young concrete substrate refers to that cured under a saturated condition for 7 days. It simulates the situation that the substrate is diagnosed unsatisfactory 7 days after casting, and a coating is needed. An old concrete substrate refers to that cured under a saturated condition for 7 days, followed by an exposure to chloride environment for a period of time (e.g. 5, 10 or 20 years).

Surface chloride, initial chloride, critical Cl$^-$ concentration and cover thickness

In this study, a constant concentration of free chloride (0.5 mol/L) is specified on the exposed surface of the concrete structures. The chosen surface chloride concentration of 0.5 mol/L is close to that in seawater with salinity of 3.5%. The initial chloride concentration in the coating and substrate is taken as 0.01 mol/L. According to the published data, the critical chloride concentration for the initiation of reinforcement corrosion falls within a broad range (0.045 to 3.22 moles of free chloride in per liter of pore solution) (Angst et al. 2009). In this study the critical chloride concentration in the pore solution is chosen to be 0.2 mol/L. The thickness of concrete cover is 30 mm. The service life of the reinforced concrete structure is defined as the time needed for the chloride concentration at the reinforcement surface (i.e., at 30 mm depth from the surface of the substrate) to reach the critical value (i.e., 0.2 mol/L). The parameters for the simulation are listed in Table 4.

Table 4 Parameters for simulating chloride transport in the coating systems.

Parameters	Symbol	Values
Initial concentration of free Cl$^-$ in coating and substrate	C_0	0.01 mol/L
Surface chloride concentration	C_s	0.5 mol/L
Exposure time	t	60 years
Critical concentration of free chloride at rebar surface	C_r	0.2 mol/L
Concrete cover	L_c	30 mm

Simulation results and discussion

Coatings with different w/c ratios (0.3, 0.4 and 0.5)

Fig. 11 shows the free chloride profiles in the uncoated substrate (Sub) and the coating-substrate systems after 50 years exposure to the chloride environment. In the coating systems, 10 mm-thick coatings with different w/c ratios (i.e. 0.3, 0.4 and 0.5) are applied on young substrates (age = 7 days). The coatings with a w/c of 0.3 can effectively reduce the chloride ingress in the substrates. However, the effectiveness of the coating decreases drastically with the increase of water-to-cement ratio. The coatings with a w/c of 0.4 or 0.5 have a very limited effectiveness to reduce the chloride ingress. The low effectiveness of the coating (w/c = 0.5) can be explained by its coarser microstructure and higher chloride diffusivity compared to the coatings with lower w/c ratios.

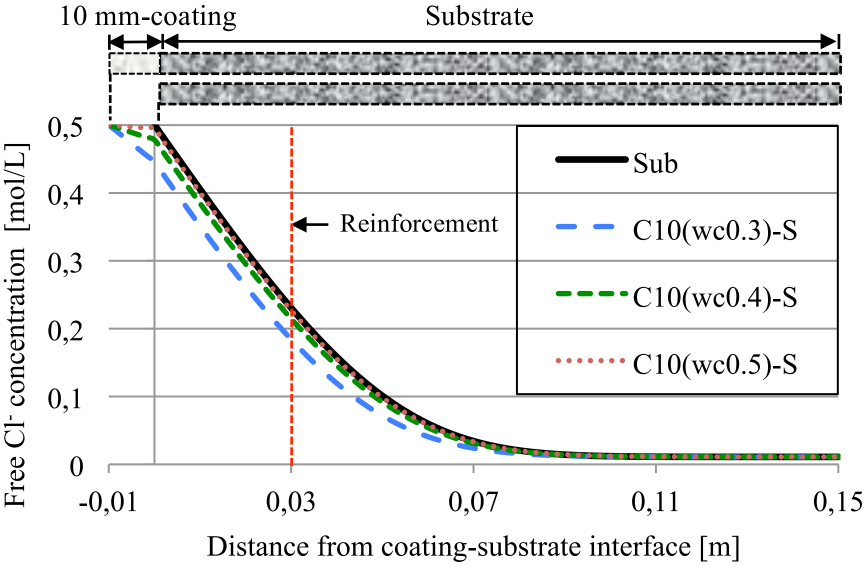
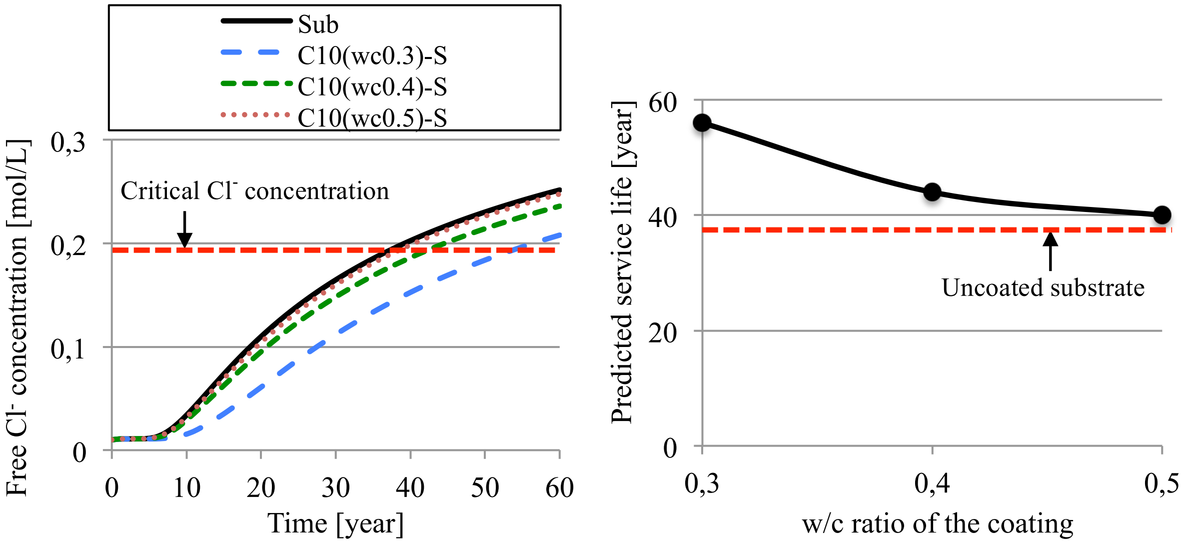


Fig. 11 Free chloride profiles in the uncoated substrate and the coating systems after 50-year exposure to the chloride environment. The 10 mm-thick coatings with different w/c ratios (i.e. 0.3, 0.4 and 0.5) are applied on young substrates.

The evolution of the concentration of free chloride at the reinforcement surface in the substrates is presented in Fig. 12a. The coatings with low w/c ratios (i.e. 0.3 and 0.4) significantly postpone the time for the concentration of free chloride at the reinforcement surface (thickness of concrete cover = 30 mm) to reach the critical value (0.2 mol/L). When a coating with a w/c of 0.5 is applied on the substrate, the evolution of the concentration of free chloride at the reinforcement surface in the coated substrate (dotted red line) almost coincides with that in the uncoated substrate (black line). Fig. 12b shows the predicted service life of the concrete structures. The extra service life of the coated substrates is 1 year (from 39 to 40 years), 5 years (from 39 to 44 years) and 17 years (from 39 to 56 years) when the coatings with a w/c of 0.5, 0.4 and 0.3 are applied, respectively. It can be concluded that the w/c ratio of the coatings plays an important role in the chloride ingress in the coating systems. To effectively protect the concrete substrate against the chloride ingress by applying a cement-based coating, a proper w/c ratio should be chosen for the coating material.



(a) Free Cl$^-$ concentration at reinforcement surface (b) Predicted service life

Fig. 12 (a) Evolution of concentration of free chloride at the reinforcement surface and (b) predicted service life of the concrete substrates. The 10 mm-thick coatings with different w/c ratios (i.e. 0.3, 0.4 and 0.5) are applied on young substrates. The original thickness of concrete cover is 30 mm.

Coatings with different thicknesses (3, 6 and 10 mm)

Fig. 13 shows the free chloride profiles in the uncoated substrate (Sub) and the coating systems after 50-year exposure. In the coating systems, coatings (w/c = 0.3) with different thicknesses (3, 6 and 10 mm) are applied on young substrates (7 days old). Not surprisingly, a thicker coating has a more pronounced effect on protecting the concrete substrate against chloride ingress.

Fig. 14a presents the evolution of the free chloride concentration at the reinforcement surface in the substrates. The coatings with different thicknesses cause a noticeable difference in the concentration of free chloride. A thicker coating (e.g. 10 mm-thick) results in a lower free chloride concentration at the reinforcement.

The predicted service life of the substrates is presented in Fig. 14b. The service life of the concrete substrate increases from 39 years to 43, 48 and 56 years by a coating (w/c = 0.3) with a thickness of 3, 6 and 10 mm, respectively. It indicates that the coating thickness has a great effect on the effectiveness of the coatings to reduce the chloride ingress in the substrates.

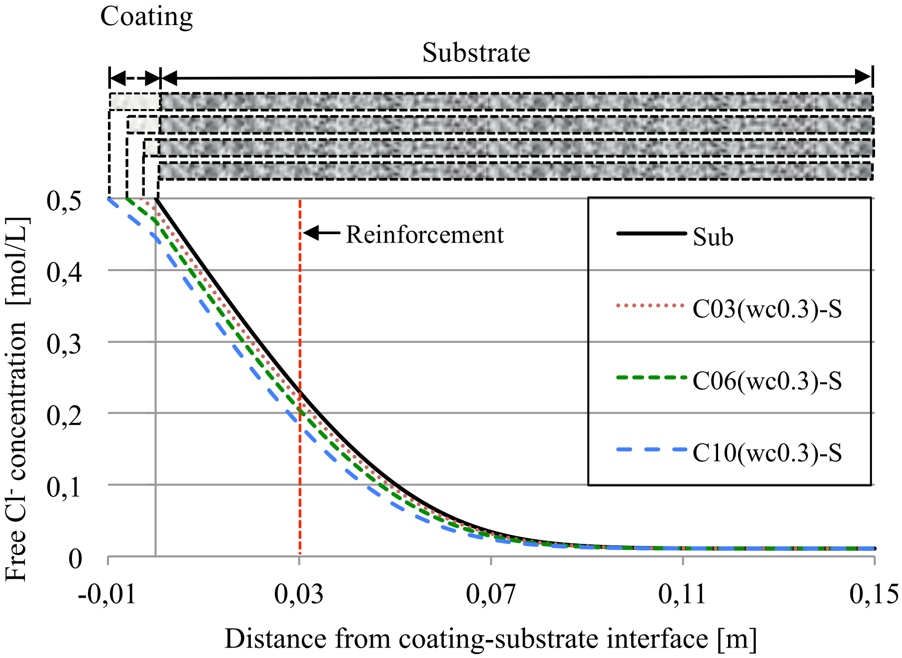
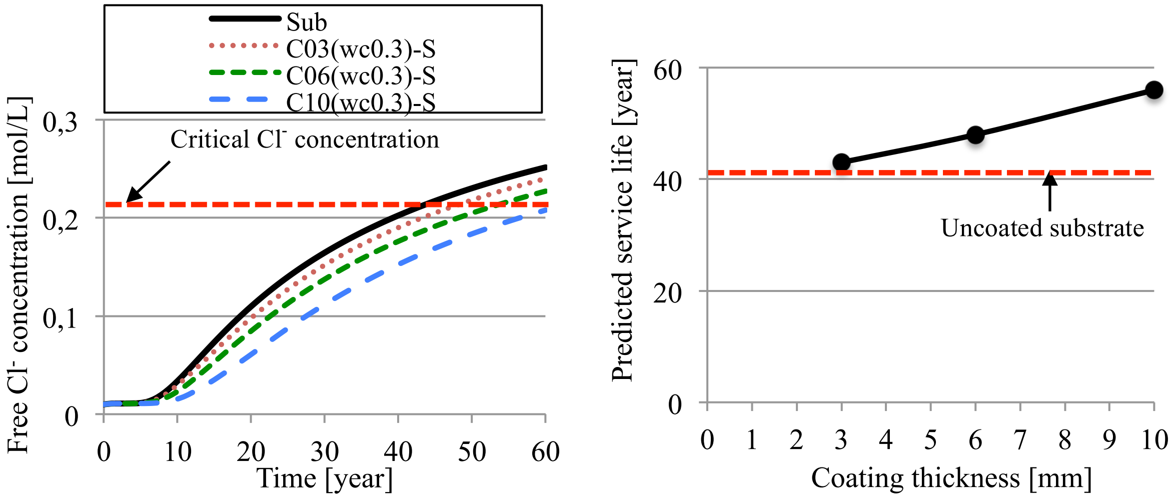


Fig. 13 Free chloride profiles in the uncoated substrate and the coating systems after 50-year exposure to the chloride environment. The coatings (w/c = 0.3) with different thicknesses (i.e. 3, 6 and 10 mm) are applied on young substrates.



(a) Free Cl$^-$ concentration at reinforcement surface (b) Predicted service life

Fig. 14 (a) Evolution of concentration of free chloride at the reinforcement surface and (b) predicted service life of the concrete substrates. The coatings (w/c = 0.3) with different thicknesses (i.e. 3, 6 and 10 mm) are applied on young substrates. The original thickness of concrete cover is 30 mm.

Coating systems with a late application of the coating (at 5, 10 and 20 years)

Fig. 15 presents the profiles of free chloride in a substrate before and after application of the coating. The uncoated substrate has been exposed to chloride environment for 10 years (the curve "10y"). After 10 years, a 10 mm-thick coating (w/c = 0.3) is applied on the substrate. Immediately after application of the coating, the concentration of free chloride in the coating material increases (see the curve "10.1y"). This increase is caused by the chloride diffusion from both the exposed surface and the substrate to the coating. After 10.1 years, more and more chloride ions are taken up from the substrate by the coating (e.g. at 11 years). In 5 years after applying the coating, the redistribution process of the chloride ions has more or less finished. As seen from the curve "15y", the chloride profile in the coating system shows a monotonic trend, and is lower than that in the uncoated substrate (Sub).

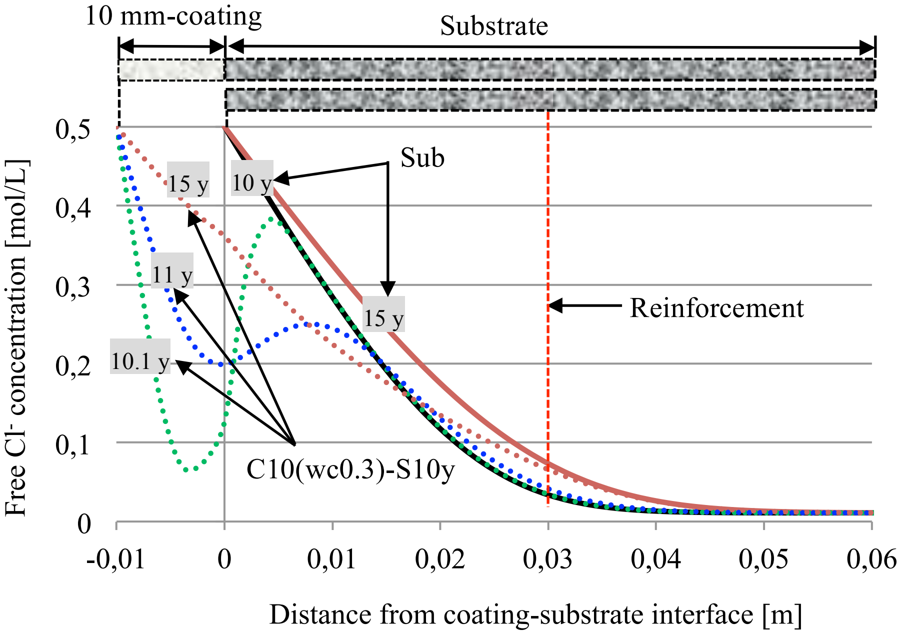


Fig. 15 Chloride profiles in the uncoated substrate and the coating system. This figure shows the chloride profiles in the uncoated substrate after 10-year exposure to the chloride envrionment. Then a 10 mm-thick coating (w/c = 0.3) is applied on the 10-year old substrate. The chloride profiles in the coating system (C10(wc0.3)-S10y) at 10.1, 11 and 15 years are presented. The profile in the uncoated substrate at 15 years (solid curve) is also presented.

Fig. 16 presents the chloride profiles in the uncoated substrate (Sub) and 4 coating systems after 50 years exposure to chloride environment. In the coating system C10(wc0.3)-S, a 10 mm-thick coating (w/c = 0.3) is applied on a young substrate. In other coating systems, the 10 mm-thick coatings (w/c = 0.3) are applied on old substrates that have been exposed to chloride environment for 5, 10 or 20 years. Fig. 16 shows that the chloride profiles in all coated substrates are lower than those in the uncoated substrate (Sub). As can be seen from the magnified illustration of chloride profiles at the steel surface (area indicated by A in Fig. 16), a late application of the coating at 20 years (C10(wc0.3)-S20y) results in a slightly higher chloride concentration in the substrate compared to the early application of the coating (C10(wc0.3)-S). Therefore, for the coatings applied on the young substrate (age = 7 days) and the old substrates (age = 5, 10, or 20 years), the application of the coatings makes only marginal difference in the free chloride profile in the substrate after 50 years exposure to the chloride environment.

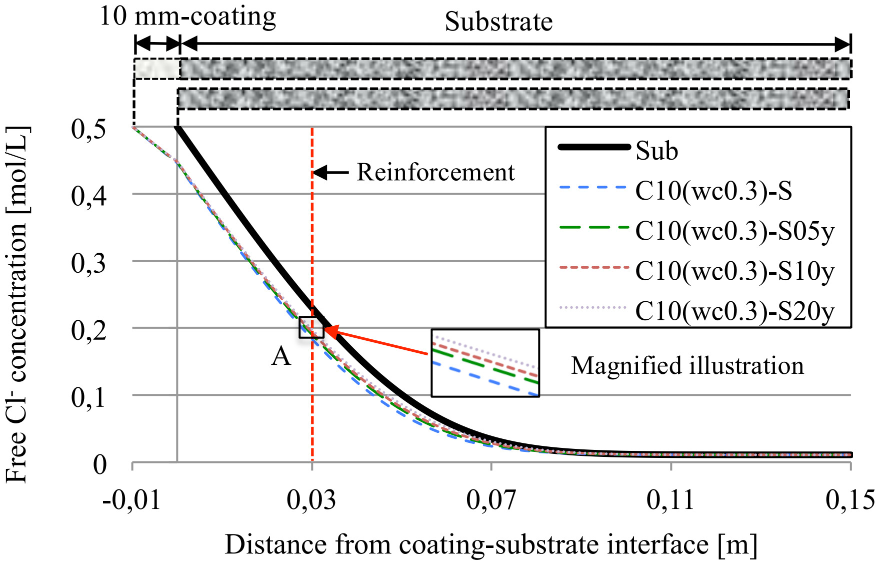
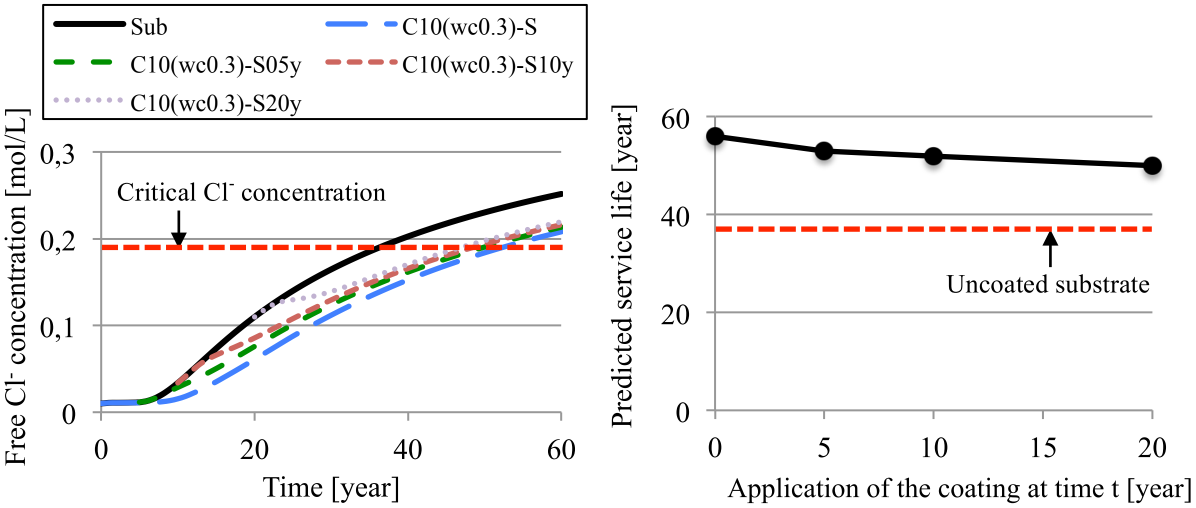


Fig. 16 Chloride profiles in uncoated substrate and coating systems after 50-year exposure to chloride environment. The coatings (10 mm-thick, w/c = 0.3) are applied on old substrates (see Table 3).

Fig. 17a presents the evolution of the concentration of free chloride at the steel surface. With an earlier application of the coating, the concentration of free chloride at the steel surface is evidently lower. The curves showing the evolution of the concentration of free chloride tend to converge over time.

Fig. 17b shows the predicted service life of the uncoated substrate and the coated substrates. The service life of the concrete structure is extended from 39 years to 56 years by an early application (i.e. at 7 days) of the coating, and to 50, 52 and 53 years by a late application of the coating at 5, 10 and 20 years, respectively. It means that a late application of the coating can still reduce the chloride ingress from the environment, but the effectiveness is lower compared to an early application. For a higher effectiveness of the coating to extend the service life of the substrate, the coating is preferably applied as early as possible to the substrate.



(a) Free Cl$^-$ concentration at reinforcement surface (b) Predicted service life

Fig. 17 (a) Evolution of concentration of free chloride at the reinforcement and (b) predicted service life of concrete substrates. The coatings (10 mm-thick, w/c = 0.3) are applied on old substrates (see Table 3).

Cost analysis of the coating materials used for extending service life of concrete structures

To give guidance to the design of coatings in practice, the cost of the coatings is analyzed in Euro/m^2/year of increased service life. Note that the cost analysis of the coatings (i.e., cement pastes) only considers the cost of materials (i.e., cement), excluding any other type of cost (e.g., construction cost). The price of the cement is taken as 2 Euro/kg according to the quotation of European cement market. Table 5 listed the cost analysis of the coatings applied on young substrates (age = 7 days). The extra service life of the coated substrate increases from 4 to 17 years if a coating (w/c of 0.3) is applied with a thickness from 3 mm (price of coating = 2.5 Euro/m^2/year) to 10 mm (cost of coating = 1.9 Euro/m^2/year). The extra service life of the coated substrate increases from 1 to 17 years if a 10 mm-thick coating is applied with a w/c ratio from 0.5 (price of coating = 24 Euro/m^2/year) to 0.3 (cost of coating = 1.9 Euro/m^2/year). It can be concluded that the effectiveness of the coatings increases with the coating thickness and a drastic increase of material cost; the effectiveness of the coatings increases with the decrease of w/c ratio and a moderate increase of material cost. To extend the service life of the substrate, a coating with a low w/c ratio is recommended, while the coating thickness should be designed depending on the requirements.

Table 5 Cost of the coating materials for extending service life of the concrete structures.

w/c ratio of substrate	Service life of uncoated substrate (years)	w/c ratio of coating	Coating thickness (mm)	Extra service life of coated substrate* (years)	Cost of coating (Euro/m^2/year of increased service life)
0.48	39	0.3	3	4	2.5
		0.3	6	9	2.1
		0.3	10	17	1.9
		0.4	10	5	5.6
		0.5	10	1	24

* The coating materials are applied on young substrates (age = 7 days).

Conclusion

The effectiveness of cement-based coatings was evaluated by simulation of chloride ingress into coated concrete substrates. In the simulation, the hydration processes of the coating and the substrate were considered. The time-dependent diffusivity and chloride binding capacity were also taken into account. The evolution of free chloride profile in the coating systems and free chloride concentration at the reinforcement is simulated. Assuming a critical chloride concentration at the reinforcement, the service life of the coated concrete structures was assessed. Parameter study was conducted to show the influence of several parameters, e.g. w/c ratio of the coating, coating thickness, and early or late application of the coating. Based on the simulation results, the following conclusions can be drawn:

- The w/c ratio of the coating plays an important role in the chloride ingress into the coating system. The service life of the uncoated substrate is 39 years. The service life of the substrates is extended by 5 and 17 years, when a 10 mm-coating with a w/c of 0.4 and 0.3 is applied, respectively. However, the chloride ingress in the substrate can be hardly affected by applying a coating with a w/c of 0.5. With this coating (w/c = 0.5), the service life of the substrate can only be extended by 1 year.
- The coating thickness is also an important parameter in chloride ingress into coated substrates. The extended service life of the substrate differs a lot when coatings with different thicknesses are applied. With a 3, 6 and 10 mm coating, the service life of the substrate can be extended by 4, 9 and 17 years, respectively.
- The cost of coating is analyzed in Euro/m^2/year of increased service life. The effectiveness of the coatings increases with the coating thickness and a drastic increase of material cost; the effectiveness of the coatings increases with the decrease of w/c ratio and a moderate increase of material cost. To extend the service life of the substrate, a coating with a low w/c ratio is recommended, while the coating thickness should be designed depending on the requirements.
- The exposure history of the substrate before applying the coating has an influence on the effectiveness of the coating. With a 10 mm coating (w/c = 0.3), the service life of the 5, 10

and 20-year old substrate can be extended by 16, 13 and 11 years, respectively. In order to protect a concrete structure exposed to the chloride environment, it is preferable to apply a coating as early as possible, since the effectiveness of the coating is reduced by a late application.

Acknowledgments

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