Analysis of time-dependent chloride diffusion in surface-treated concrete based on a rapid numerical approach

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ABSTRACT

Reinforcement corrosion induced by chloride penetration is a major threat to reinforced concrete structures in marine environments. The use of surface treatments to improve the durability of reinforced concrete structures has drawn increasing attention in recent decades due to their cost-effectiveness and convenience in construction. However, current knowledge of a practical, durable design to protect surface-treated concrete structures from chloride-induced steel corrosion remains insufficient. On this account, a rapid numerical approach was developed in this study to analyse the chloride diffusion in bilayer materials. In this approach, the time-dependency was considered for the chloride diffusion coefficients of both the surface-treated layer and the underlying concrete substrate and for the surface chloride content. The validity of this approach was verified with the finite element method and the computation time was only one hundred-thousandth that of the latter. This proposed approach makes it feasible in practice to estimate the probability of corrosion initiation in surface-treated concrete structures via Monte Carlo simulation.

Keywords: Chloride content; diffusion process; surface-treated concrete; steel corrosion; rapid numerical approach; time-dependence; probability of corrosion initiation.

Nomenclature

$f_n(x,\lambda_n)$	Trigonometric function
$f_n^i\left(x_l,\lambda_n\right)$	Trigonometric function at step i
$g_n(x,\lambda_n)$	Trigonometric function
h_1	Thickness of surface-treated layer
h_2	Thickness of concrete substrate
p_t	Intermediate variable
t_{st}	Initial exposure time
t_{ex}	Final exposure time
t_0	Reference age of concrete
t_i^{cal}	Calculation point at time step i
t_i	Series time points
$\tan_1$	Tangent function of P_1
$\tan_2$	Tangent function of P_2
X	Concrete depth of interest
x_l	Depth at point l
A_n, B_n, A_n', B_n'	Coefficients
$A_n^{\prime,i}$	Coefficient at step i
$C(x,T)$	Chloride content
$\overline{C}(x)$	Accumulated chloride content
$\overline{C^{i-1}}(x)$	Accumulated chloride content at step $(i-1)$
$C_T^{x=0}$	Surface chloride content

$C_{st}^{x=0}$	Initial surface chloride content
$C_{u}^{x=0}$	Ultimate surface chloride content
$C_{i}^{x=0}$	Chloride content at step *i*
C_{cri}	Critical chloride content for corrosion initiation
$C_{X_L,l}^{N,M}$	Chloride content at point *l* when the number of characteristic roots is *N*, the number of steps is *M* and the depth interval is X_L
$C_{0.1,l}^{50,50}$	Chloride content at point *l* when the number of characteristic roots is 50, the number of steps is 50 and the depth interval is 0.1
$D_{t_0,1}$	Chloride diffusion coefficient of surface-treated layer at age t_0
$D_{t_0,2}$	Chloride diffusion coefficient of concrete substrate at age t_0
$Err_{X_L}^{N,M}$	Relative error when the number of characteristic roots is *N*, the number of steps is *M* and the depth interval is X_L
L	Number of points
N	Number of characteristic roots
M	Number of steps
P_1	Larger period amplification coefficient
P_2	Smaller period amplification coefficient
P_{cr}(t)	Possibility of corrosion initiation at time *T*
T	Considered exposure time
X_L	Depth interval
W_l	Weighted factor at point *l*
α_1	Aging factor for chloride diffusion coefficient $D_{t_0,1}$

α_2	Aging factor for chloride diffusion coefficient $D_{t_0,2}$
β	Aging factor of surface chloride content
λ_n	Characteristic root
$\varphi_1(T)$	Time-dependency of chloride diffusion coefficient $D_{t_0,1}$
$\varphi_2(T)$	Time-dependency of chloride diffusion coefficient $D_{t_0,2}$

1. Introduction

Chloride-induced corrosion of reinforcement is one of the major threats to reinforced concrete (RC) structures in marine environments. The annual cost of infrastructure corrosion was reported to reach 22.6 billion US dollars in 2002 in the United States alone (Koch et al., 2002). Protective surface treatment is a method used to significantly delay the onset of chloride-induced steel corrosion and the subsequent corrosion rate in RC structures. The application of surface treatment to RC structures has gained increasing popularity both for protection of newly built RC structures and for upgrading of existing structures (Almusallam et al., 2003; Dai et al., 2010; JSCE-325, 2006). The ease of application has been particularly attractive to the construction industry (Basheer et al., 1998; Ibrahim et al., 1997; Ibrahim et al., 1999; Nanukuttan et al., 2008; Raupach & Wolff, 2003; Schueremans et al., 2007; Swamy et al., 1995; Zhan et al., 2003).

Protective surface treatments can generally be classified into three categories: surface coating, sealing and surface impregnation (Dai et al., 2010). Unlike conventional concrete, surface-treated concrete is, in fact, a bilayer material composed of a surface-treated layer and a concrete substrate. Considerable laboratory and field studies have been conducted to study the diffusion process in surface-treated concrete (Basheer et al., 1998; Ibrahim et al., 1997; Ibrahim et al., 1999; Nanukuttan et al., 2008; Raupach & Wolff, 2003; Schueremans et al., 2007; Swamy et al., 1995; Zhan et al., 2003). Some researchers have investigated surface-treated concrete in the same way as untreated concrete for the sake of simplicity (Medeiros & Helene, 2009; Sadati et al., 2015). In contrast, Zhang & Buenfeld (2000) proposed a numerical model to calculate the chloride profile in a surface-treated concrete using the finite difference method. However, both the methods are not suitable for characterizing and modelling the chloride resistance of surface-treated concrete because they do not solve the mathematical problem of chloride diffusion in bilayer materials.

On the other hand, considerable works have been made on the diffusion process in bilayer materials in other research fields. Jaeger & Carslaw (1959) deduced an analytical solution of bilayer diffusion for heat conduction in solids. Crank (1979) subsequently derived a similar solution for mass transport in composite materials. Pontrelli & Monte (2007) proposed a numerical method of bilayer diffusion for drug-eluting stents. Although these approaches do not consider a time-dependency of the diffusion process, they provide a mathematical basis for further investigating the long-term chloride diffusion process in surface-treated concrete.

In practical design, surface treatments have usually been regarded as an additional protective measure for the durability of concrete structures, but the service life of concrete structures has rarely been assessed in a quantitative manner. Because surface treatments increase the construction cost, it is highly desirable for decision-makers (e.g. the owner) to know how much a surface treatment can reduce the maintenance cost as to achieve an optimal maintenance strategy for concrete structures during their service life. One prerequisite to realise this is the quantitative prediction of chloride ingress in surface-treated concrete. It should also be noted that the chloride ingress process in surface-treated concrete structures actually involves great uncertainties and randomness due to the variability in material properties (e.g. the chloride diffusion coefficient of concrete), the variability in geometry (e.g. the cover depth and the surface-treated layer thickness) and the random nature of the marine environment (e.g. the surface chloride content). Moreover, concrete structures undergo continuous deterioration due to various environmental and loading actions. Therefore, it is considered reasonable to adopt a probabilistic approach rather than a deterministic one when predicting the time-dependent chloride ingress process in surface-treated concrete. It should be noted that considerable efforts have been made to assess the impact of degradation on the time-dependent performance of various structures, e.g. concrete bridges (Biondini et al., 2014; Enright & Frangopol, 1998; Zanini et al., 2017; Zanini et al., 2013; Zanini et al., 2020) and marine concrete structures (Bentz, 2003; Duan et al., 2014; Zanini et al., 2017), based on probabilistic approaches. However, there is little work on the assessment of the effect of deterioration on a surface-treated concrete.

The finite element method (FEM) is a generic way to predict chloride ingress in structures with various material properties, geometries and boundary conditions. However, the FEM is usually time-consuming, and probabilistic analyses may require millions of samples (e.g. based on Monte Carlo simulation) to achieve convergent results, which makes the FEM inapplicable in engineering practice. Therefore, it is desirable to develop a computationally efficient approach for the prediction of chloride diffusion in bilayer materials.

An explicit analytical solution was recently proposed by the authors to analyse the diffusion process in bilayer materials (Dai & Wang, 2015). However, the time-dependency was assumed to take a specific form for the two layers of materials in the solution, and the analysis was carried out in a deterministic manner. Thus, this solution has some limitations in engineering applications, such as in repairs of concrete structures with surface treatments, for which the time-dependencies of the repair layer and the original substrate may differ. The objective of this study was to develop a rapid numerical approach (RNA) for the prediction of chloride ingress in bilayer materials that considers the time-dependency of the chloride diffusion coefficients of both layers of materials. This approach could also consider the time-dependency of the surface chloride content. Compared with the FEM, the proposed method will lead to an enormous reduction in computation time and thus facilitate the probability analysis of steel reinforcement corrosion in surface-treated concrete structures in an efficient manner. It should be noted that only liquid silane, silane-based cream and silane-based gel are considered in this study. These penetrants line the pores of concrete to render it hydrophoc. As a result, the pores of the surface concrete are not water filled, and chloride diffusion is slowed down effectively. From a mathematical point of view, this effect can be modeled as an equivalent surface-treated layer with decreased chloride diffusion coefficient.

2. Analytical solution for chloride diffusion in bilayer materials with constant chloride diffusion coefficients

Figure 1 shows a typical surface-treated RC specimen. The concrete comprises two layers, a surface-treated layer and a concrete substrate (Zhang et al., 1998). Because the concrete specimen usually has a sufficiently large thickness, a half symmetric model can be used for analysis for the sake of simplicity. An explicit solution for chloride diffusion in such a bilayer material was previously developed by the authors (Dai & Wang, 2015). Figure 1 shows the chloride diffusion model, in which the thickness and the chloride diffusion coefficient at age t_0 are h_1 and $D_{t_0,1}$ for the first layer and h_2 and $D_{t_0,2}$ for the second layer, respectively. According to Fick's second law, the chloride content $C(x,T)$ satisfies the following differential equations

$$\frac{\partial C(x,T)}{\partial T} = D_{t_0,1}\frac{\partial^2 C(x,T)}{\partial x^2}, \text{ for } 0 \le x \le h_1 \tag{1}$$

$$\frac{\partial C(x,T)}{\partial T} = D_{t_0,2}\frac{\partial^2 C(x,T)}{\partial x^2}, \text{ for } h_1 \le x \le h_1 + h_2, \tag{2}$$

where x is the concrete depth of interest and T is the considered exposure time. The initial and boundary conditions are specified as

$$C(x,T)\big|_{T=0} = \overline{C}(x), \text{ for } 0 \le x \le h_1 + h_2 \tag{3}$$

$$C(x,T)\big|_{x=0} = C_T^{x=0}, \text{ for } T \ge 0 \tag{4}$$

$$\left.\frac{\partial C(x,T)}{\partial x}\right|_{x=h_1+h_2} = 0, \; C(x,T)\big|_{x=h_1+h_2} = 0, \text{ for } T \ge 0, \tag{5}$$

where $\overline{C}(x)$ is the initial chloride content in the bilayer material and $C_T^{x=0}$ is the surface chloride content at time T. Equation (5) assumes that no chloride transport occurs beyond the right edge of the model ($x=h_1+h_2$) because the concrete thickness is usually large enough as compared to the chloride diffusion depth. This boundary condition could be verified by checking if the chloride content at right boundary is sufficient low. The continuity conditions at $x = h_1$ are assumed to be

$$C(x,T)\big|_{x=h_1^-} = C(x,T)\big|_{x=h_1^+} \tag{6}$$

$$D_{t_0,1}\left.\frac{\partial C(x,T)}{\partial x}\right|_{x=h_1^-} = D_{t_0,2}\left.\frac{\partial C(x,T)}{\partial x}\right|_{x=h_1^+} \tag{7}$$

Figure 1. Dimensions and chloride diffusion coefficients of surface-treated RC specimen.

Based on the method of separation of variables, the solutions to Equations (1) and (2) can be expressed as

$$C\left(x,T\right)=\begin{cases} C_T^{x=0}+\left[A_n\sin\left(\lambda_n x/\sqrt{D_{t_0,1}}\right)+B_n\cos\left(\lambda_n x/\sqrt{D_{t_0,1}}\right)\right]\exp(-\lambda_n^2 T) & 0\le x\le h_1 \\ C_T^{x=0}+\left\{A_n'\sin\left[\lambda_n\left(x-h_1\right)/\sqrt{D_{t_0,2}}\right]+B_n'\cos\left[\lambda_n\left(x-h_1\right)/\sqrt{D_{t_0,2}}\right]\right\}\exp(-\lambda_n^2 T) & h_1\le x<h_1+h_2 \end{cases}, \quad (8)$$

where A_n, B_n, A_n' and B_n' are four coefficients to be determined and λ_n is the characteristic root. With the initial condition of (3), the boundary conditions of (4) and (5) and the continuity conditions of (6) and (7), it is easily shown that $C(x,T)$ is obtained as

$$C\left(x,T\right)=C_T^{x=0}+\sum_{n=1}^{\infty}A_n' f_n(x,\lambda_n)\exp(-\lambda_n^2 T), \quad (9)$$

where $f_n(x,\lambda_n)$ and A_n' are respectively defined as

$$f_n(x,\lambda_n)=\begin{cases} \dfrac{\cot\left(\lambda_n h_2/\sqrt{D_{t_0,2}}\right)}{\sin\left(\lambda_n h_1/\sqrt{D_{t_0,1}}\right)}\sin\left(\lambda_n x/\sqrt{D_{t_0,1}}\right) & 0\le x\le h_1 \\ \dfrac{1}{\sin\left(\lambda_n h_2/\sqrt{D_{t_0,2}}\right)}\cos\left[\lambda_n\left(x-h_1-h_2\right)/\sqrt{D_{t_0,2}}\right] & h_1\le x<h_1+h_2 \end{cases} \quad (10)$$

$$A_n'=\int_0^{h_1+h_2}[\bar{C}(x)-C_T^{x=0}]f_n(x,\lambda_n)dx\Big/\int_0^{h_1+h_2}f_n^2(x,\lambda_n)dx, \quad (11)$$

and λ_n satisfies the following characteristic equation

$$\tan(\lambda_n h_1/\sqrt{D_{t_0,1}})\tan(\lambda_n h_2/\sqrt{D_{t_0,2}})=\sqrt{D_{t_0,1}/D_{t_0,2}} \quad (12)$$

The determination of A_n' and λ_n will be explained in section 4. The initial chloride content $\bar{C}(x)$ is considered in the determination of A_n' (Equation (11)).

3. Modelling strategy for bilayer materials with time-dependent chloride diffusion

coefficients

It should be noted that the analytical solution of Equation (9) is only valid for bilayer materials with a constant chloride diffusion coefficient in each layer. However, the real situation of surface-treated concrete in a chloride environment is more complicated.

Because the concrete structure undergoes continuous deterioration due to the combination of environmental and loading actions (Maekawa et al., 2008), such as thermal- or shrinkage-induced cracking and frost damage, the chloride diffusion coefficient of surface-treated layer may increase over time. It should be noted that the treated concrete is still expected to perform better than untreated concrete even after degradation. On the other hand, the porosity and chloride diffusion coefficient of the concrete substrate decrease as cement hydration proceeds (Maekawa et al., 2008; Pack et al., 2010). In other words, the transport properties of the two materials may exhibit totally different time-dependencies, as shown in Figure 2a, which should be considered in the mathematical solution.

Figure 2. Schematic diagram: (a) time-dependent D_1 and D_2 and (b) approximate representation of D_1 and D_2 with step function.

A feasible and practical way to solve the above-mentioned problem is to approximate the time-dependent development by a step function, as shown in Figure 2b. Because the chloride diffusion coefficient is approximated as a constant in each time step, the analytical solution can be used. Thus, the numerical solution will better approach the correct result as the number of time steps increases. However, some problems should be solved before this modelling strategy can be adopted:

1. How can the time-dependent chloride diffusion coefficients be determined with the step function?
2. How can the time-dependent surface chloride content and chloride diffusion coefficients be considered simultaneously?
3. How can the characteristic roots λ_n of Equation (12) be solved rapidly?
4. How can the chloride content accumulated in the previous steps be considered in the current step?

To address these questions, an RNA is developed below and verified with the FEM.

4. Solution for chloride diffusion in bilayer materials with time-dependent chloride diffusion coefficients

4.1 Approximate representation of chloride diffusion coefficient

Without loss of generality, the time-dependent chloride diffusion coefficients can be expressed as

$$D_1 = D_{t_0,1} \cdot \varphi_1(T),\ D_2 = D_{t_0,2} \cdot \varphi_2(T) \tag{13}$$

where $\varphi_1(T)$ and $\varphi_2(T)$ are a function of time T, as shown in Figure 3a. $\Phi(T)$ is defined as the ratio between $\varphi_1(T)$ and $\varphi_2(T)$, i.e.,

$$\Phi(T) = \varphi_1(T)/\varphi_2(T) \tag{14}$$

Because $\Phi(T)$ represents the relative difference in time-dependency between the two materials, as shown in Figure 3a, it can be used as an index to determine the chloride diffusion coefficients with a step function. In view of the nonlinearity of $\Phi(T)$ with time, the approximate representation of $\Phi(T)$ with a step function is better than the use of a constant time interval, as shown in Figure 3b. Although there is a specific point at each step that would introduce zero error according to the mean value theorem, it is time-consuming to find this point in practice. Therefore, the midpoint t_i^{cal} at each step is chosen as the calculation point in this study considering a balance between accuracy and efficiency, as shown in Figure 3b.

4.2 Surface chloride content

In general, the surface chloride content $C_T^{x=0}$ is time-dependent, as shown in Figure 3c (Costa & Appleton, 1999). To obtain the chloride content in bilayer materials, a numerical approximation method based on the superposition principle is adopted in this study (Maheswaran & Sanjayan, 2004). Like the chloride diffusion coefficient, the time-dependency of the surface chloride content is approximated by a step function with the same time steps, as shown in Figure 3b and d. To ensure that there is no loss of chloride content in the approximation, the surface chloride content $C_i^{x=0}$ at each step is selected so that area A_1 is equal to area A_2, as shown in Figure 3d.

Figure 3. Numerical algorithms adopted in modelling strategy: (a) time-dependent $\Phi(T)$, (b) approximate representation of $\Phi(T)$ with step function, (c) time-dependent $C_T^{x=0}$ and (d) approximate representation of $C_T^{x=0}$ with step function.

4.3 Solution algorithm for characteristic root λ_n

The computational efficiency of the RNA is dependent on the solution algorithm for the characteristic root λ_n. Therefore, it is essential to explore an efficient way for the determination of λ_n.

Equation (12) is a product of two tangent functions with respect to two period amplification coefficients $h_1/\sqrt{D_{t_0,1}}$ and $h_2/\sqrt{D_{t_0,2}}$. For the sake of convenience, it is assumed that P_1 and $\tan_1$ are the bigger period amplification coefficient and tangent function (i.e., if $h_1/\sqrt{D_{t_0,1}} \geq h_2/\sqrt{D_{t_0,2}}$, P_1 is $h_1/\sqrt{D_{t_0,1}}$ and $\tan_1$ is $\tan(\lambda_n h_1/\sqrt{D_{t_0,1}})$). Thus, Equation (12) can be rewritten as

$$\tan_1(\lambda_n P_1)\tan_2(\lambda_n P_2) = \sqrt{D_{1,i}^{cal}/D_{2,i}^{cal}}, \tag{15}$$

where $D_{1,i}^{cal}$ and $D_{2,i}^{cal}$ are the chloride diffusion coefficients of the first and second layers at the calculation point t_i^{cal}, respectively, as shown in Figure 3b.

Obviously, the right-hand side of Eq. (15) is always positive. For any negative semi-period region of $\tan_1$ (Fig. 4a), i.e. $(2k-1)\pi/2 = \lambda_{l,1}P_1 \leq \lambda_n P_1 \leq \lambda_{r,1}P_1 = k\pi, k = 1, 2, 3...$, the characteristic root exists only when $\tan_2$ is also negative, (i.e. potential solution region $\lambda_l \leq \lambda_n \leq \lambda_r$), as shown in Fig. 4a to c; otherwise, there is no root, as shown in Fig. 4d. The same is true for the positive semi-period region of $\tan_1$. Because the tangent function is monotonic in each semi-period region, it is easily inferred that each semi-period region contains only one root. Therefore, the characteristic roots can be easily determined by searching each semi-period region of $\tan_1$ with numerical methods (Fig. 4), such as a binary search. It should be noted that for case 3 shown in Fig. 4c, a numerical difficulty may occur because $\tan_2$ changes too rapidly near the vertical asymptotic line. In this case, the convergence condition can be changed to the length of the solution region instead of the relative error of Eq. (15).

Figure 4. Identification of solution region for (a) case 1, (b) case 2, (c) case 3 and (d) case 4.

4.4 Accumulated chloride content

As discussed above, the chloride content accumulated in the previous steps should be considered in the current step. This can be achieved by adjusting A_n' in Equation (11) according to the existing chloride content $\bar{C}(x)$. More specifically, $A_n'^{,i}$ at the i^{th} step can be obtained by substituting the chloride profile $\overline{C^{i-1}}(x)$ at the last step into Equation (11) and then integrating point by point as follows

$$\begin{aligned} A_n'^{,i} &= \int_0^{h_1+h_2} [\bar{C}(x) - C_T^{x=0}] f_n^i(x,\lambda_n)dx \Big/ \int_0^{h_1+h_2} \left(f_n^i(x,\lambda_n) \right)^2 dx \\ &\approx \sum_l^L \left[\overline{C^{i-1}}(x_l) - C_i^{x=0} \right] f_n^i(x_l,\lambda_n)\Delta x \Big/ \int_0^{h_1+h_2} \left(f_n^i(x,\lambda_n) \right)^2 dx \end{aligned}, \tag{16}$$

where x_l is the specimen depth at the l^{th} point, L is the total number of points, $f_n^i(x_l,\lambda_n)$ is the trigonometric function at the i^{th} step, and Δx is the interval.

Figure 5. Supplementary solution to improve convergence: (a) numerical error near the right border, (b) case with depth interval 0.7 mm and (c) case with depth interval of 0.9 mm.

Figure 5a shows a comparison of different depth intervals Δx (case T8 in Table 1). Some errors can be seen near the right border of the region because $A_n'^{,i}$ of Equation (16) is approximate rather than exact. It is also difficult to determine whether the depth interval is sufficiently accurate before calculation. More importantly, a smaller depth interval results in a higher computational cost, which is unfavourable for probability analysis based on Monte Carlo simulation. Therefore, a supplementary scheme is proposed as follows. Because the concrete specimen usually has a sufficiently large thickness, the chloride content at the right border can be assumed to be equal to the initial chloride content. Thus, the chloride content at any point in the error region is simply determined by linear interpolation between the chloride content at the left point of the error region and the initial chloride content, as shown in Figure 5a. In this study, all initial chloride contents are zero. After modification, the chloride content profile is significantly improved, as shown in Figure 5b and c.

Table 1 Values of all parameters used for validation of proposed model.

5. Convergence analysis

It is expected that the computational accuracy of the proposed model increases as the number of characteristic roots N and the number of steps M increase but the depth interval Δx decreases. Therefore, it is desirable to determine reasonable values for these parameters via convergence analysis.

Figure 6 shows the convergence analysis for case T8 (Table 1) as an example. For the sake of convenience, a relative error $Err_{X_L}^{N,M}$ is defined to evaluate the effects of N, M and Δx on the convergence of the model

$$Err_{X_L}^{N,M} = \sum_{l}^{1300} W_l \frac{abs\left(C_{X_L,l}^{N,M} - C_{0.1,l}^{50,50}\right)}{C_{0.1,l}^{50,50}} \tag{17}$$

$$W_l = \frac{C_{0.1,l}^{50,50}}{\sum_{l}^{1300} C_{0.1,l}^{50,50}} \tag{18}$$

where W_l is the weighted factor at the l^{th} point, $C_{X_L,l}^{N,M}$ is the chloride content at the l^{th} point when the number of characteristic roots, the number of steps and the depth interval are N, M and Δx, respectively, and $C_{0.1,l}^{50,50}$ is the chloride content at the l^{th} point when $N = 50$, $M = 50$ and $\Delta x = 0.1$. $C_{0.1,l}^{50,50}$ is assumed to be the 'correct' result for comparison.

Figure 6 Effects of (a) number of characteristic roots, (b) number of time steps and (c) depth interval on computational accuracy.

Figure 6 shows that the relative error decreases sharply as N increases. When N is equal to 10, the relative error is less than 2%. A similar trend is observed for the number of time steps, but the relative error decreases more gradually. In contrast, the relative error fluctuates up and down as Δx decreases. When Δx is equal to 1 mm, the relative error is less than 2%. Therefore, in all the following computations, $N = 10$, $M = 10$ and $\Delta x = 1$ mm.

6. Model validation

6.1 Simple cases

To validate the proposed RNA, eight cases (i.e., T1 to T8 in Table 1) with different parameters are considered. The time-dependencies of the chloride diffusion coefficients of both materials are the same in T1 to T4 but differ in T5 to T8. In all the cases (T1 to T8), the chloride diffusion coefficients are given by

$$D_1 = D_{t0,1}\left(\frac{t_{st}+T}{t_0}\right)^{-\alpha_1},\ D_2 = D_{t0,2}\left(\frac{t_{st}+T}{t_0}\right)^{-\alpha_2} \tag{19}$$

The series time point t_i and the calculation time point t_i^{cal} are specified as

$$t_i = t_0\left[\frac{i}{m}p_t + \left(\frac{t_{st}}{t_0}\right)^{\alpha_2-\alpha_1}\right]^{\frac{1}{\alpha_2-\alpha_1}} - t_{st} \qquad i = 0,1\cdots m \tag{20}$$

$$t_i^{cal} = t_0\left[\frac{2i-1}{2m}p_t + \left(\frac{t_{st}}{t_0}\right)^{\alpha_2-\alpha_1}\right]^{\frac{1}{\alpha_2-\alpha_1}} - t_{st} \qquad i = 1,2\cdots m\,, \tag{21}$$

where p_t is defined as

$$p_t = \left(\frac{t_{st}+t_{ex}}{t_0}\right)^{\alpha_2-\alpha_1} - \left(\frac{t_{st}}{t_0}\right)^{\alpha_2-\alpha_1} \tag{22}$$

In Equations (20) to (22), t_0 is the reference age of concrete, and t_{st} and t_{ex} are the initial and final exposure times, respectively. The time-dependency of the surface chloride content is assumed to be given by

$$C_T^{x=0} = C_{st}^{x=0} + C_u^{x=0}(1-e^{-\beta T}) \tag{23}$$

where $C_{st}^{x=0}$ is the initial surface chloride content, $C_u^{x=0}$ is the ultimate surface chloride content and β is the aging factor of the surface chloride content. Thus, the surface chloride content $C_i^{x=0}$ at each step, as shown in Figure 3d, is equal to

$$C_i^{x=0} = C_{t_{st}}^{x=0} + C_u^{x=0} + \frac{C_u^{x=0}\left(e^{-\beta t_i} - e^{-\beta t_{i-1}}\right)}{\beta\left(t_i - t_{i-1}\right)} \tag{24}$$

Table 1 summarises the value of each parameter used in the analysis. The analytical prediction is compared with the FEM (Thompson, 2005), where the element length and the time step are taken as 0.4 mm and 0.1 day, respectively. The numerical results are shown in Figure 7, which demonstrates a good agreement between them and therefore verifies the validity of the RNA. In addition, the computational times (CPU Intel i5-8265U, 1.60 GHz) for the RNA and the FEM are also listed in Table 2, which indicates that the computational time is greatly reduced with the RNA (by a factor ranging from 10,000 to 100,000).

Figure 7 Numerical verification of proposed model for simple cases: (a) T1, (b) T2, (c) T3, (d) T4, (e) T5, (f) T6, (g) T7 and (h) T8.

Table 2 Comparison of computational time between FEM and RNA.

6.2 Repair case

In the eight simple cases discussed above, the time-dependency of the surface-treated layer is assumed to remain invariable throughout the service period. However, real situations may be more complicated. One situation is the repair of concrete structures, after which the chloride diffusion coefficient of the surface-treated layer is significantly reduced.

Because the RNA can analyse any chloride diffusion process, one repair case is further studied, as shown in Figure 8a, in which the surface treatment effect is assumed to be completely lost after a certain period (i.e., the diffusion coefficient of the surface-treated layer becomes the same as that of the concrete substrate). Phases 1 and 2 (Figure 8a) take 5 and 10 steps, respectively. The other parameters are the same as those adopted in the previous simple case (i.e., T8 in Table 1).

Figure 8 Numerical verification of proposed model for repair case T8: (a) schematic illustration of diffusion coefficient and (b) numerical result of chloride profile.

A comparison between the RNA and the FEM for these complicated cases is shown in Figure 8b, which again demonstrates a good agreement between them. Therefore, the validity of the proposed model is further verified.

7. Comparison between RNA model and saltwater immersion tests

Although considerable effort has been devoted to quantifying the diffusion parameters of surface-treated concrete by saltwater immersion tests (Basheer et al., 1998; Ibrahim et al., 1997; Ibrahim et al., 1999; Nanukuttan et al., 2008; Raupach & Wolff, 2003; Schueremans et al., 2007; Swamy et al., 1995; Zhan et al., 2003), only a limited number of studies have reported on their theoretical prediction. In this section, the experimental data from two saltwater immersion tests are analysed quantitatively with the RNA.

7.1 Comparison between RNA model and Zhan et al.'s chloride immersion test

Zhan et al. (2005) investigated the efficacy of surface-treatment by a saltwater immersion test. They casted two series of cube concrete specimens (100 mm) of water-cement ratios (w/c) of 0.4 and 0.6. The samples were first cured at a relative humidity of

99% and a temperature of 20 ℃ for 14 days and subsequently cured at a relative humidity of 50% and a temperature of 20 ℃ for another 42 days. Silane-based cream and gel were used. The water-repellent depths were measured by Fourier-transform infrared spectroscopy, as summarized in Table. 3. Figure 9 shows the chloride content profiles in untreated and surface-treated concretes after 28-day immersion in a 3% NaCl solution. More experimental details can be found in Zhan et al. (2005).

It should be noted that only liquid silane, silane-based cream and silane-based gel are considered in this study. These penetrants line the pores of concrete to render it hydrophocity. As a result, the pores of the surface concrete are not water filled, and chloride diffusion is slowed down effectively. From a mathematical point of view, this effect can be modeled as an equivalent surface-treated layer with decreased chloride diffusion coefficient. To determine the surface chloride content and the chloride diffusion coefficients of the surface-treated layer and the concrete substrate, a least-squares analysis is conducted based on the RNA. Table 3 lists the regression results. The time-dependency is also ignored in this analysis for the sake of simplicity because these tests lasted only 28 days.

The regression analyses show that the chloride diffusion in the surface-treated concrete is close to that in the untreated concrete (Table 3), especially for the case of 0.4 water-cement ratio. The chloride diffusion coefficient of the surface-treated layer is considerably lower than that of the concrete substrate, which is in line with the previous experimental observations (Dai et al., 2010). This shows that the RNA could be applied to the immersion test of surface-treated concrete to determine the diffusion coefficients of the surface-treated layer and the concrete substrate. More importantly, only 2 to 3 minutes were needed for each analysis.

Figure 9 Figure 10. Regression analysis of Zhan et al.'s (2005) saltwater immersion test for (a) case of w/c=0.4 and (b) case of w/c=0.6.

Table 3 Regression results for surface-treated concrete specimens of Zhan et al.'s (2005) saltwater immersion test.

7.2 Comparison between RNA model and Wang's chloride immersion test

Two concrete cylinderical samples collected from a concrete port (Wang, 2014), which was built in Shenzhen, China in 2014, and another two from the laboratory are presented here to assess the validity of the developed model on saltwater immersion test. B26 and P34 were the two core samples collected from the above-mentioned port, with water-binder ratio 0.45. Fly ash and slag were both added to improve the chloride ion penetration resistance (for both fly ash and slag the replacement level was 30%). Liquid silane (500 g/m^2) was used as a surface protective approach to enhance the durability of the concrete. On the other hand, while samples C1 and C2 were two specimens cast in the authors' laboratory with the same mixture as that of the concrete used to construct the port facilities (Wang, 2014). The two laboratory specimens were first water cured for 28 day. To improve the penetration depth of liquid silane, the two laboratory specimens were subsequently pre-dried at 60 °C for two weeks. The same surface treatment approach as applied for the concrete port was then applied (i.e. 500 g/m^2 liquid silane) on C1 and C2 samples.

The above four specimens (B26, P34, C1 and C2) were immersed in saltwater (NaCl

5%) for 180 days. After the immersion test, all the specimens were split into two halves. Pure water was sprayed on the broken surfaces and the thicknesses of the surface-treated layer were measured by a colorimetric method (Figure. 10).

Figure 11 Measurement of thickness of the surface-treated layer by colorimetric method.

Figure 11 shows the chloride content profiles in four surface-treated concrete specimens. Table 4 lists the average thicknesses of the surface-treated layers of the four specimens. A least-squares analysis was conducted based on the RNA to determine the surface chloride content and the chloride diffusion coefficients of the surface-treated layer and the concrete substrate. The time-dependency was ignored in the analysis for the sake of simplicity.

Table 4 Regression results for surface-treated concrete specimens of Wang's (2014) saltwater immersion test.

Figure 12 Regression analysis of saltwater immersion test for samples (a) C1, (b) C2, (c) B26 and (d) P34.

The regression results are summarised in Table 4. Figure 11 shows a comparison between the experimental results and the regression results, which demonstrates a good agreement between them. The average diffusion coefficient of the concrete substrate is 3.55×10^{-12} m^2/s, which is in line with the previous experimental observations of blended concrete (Saeki et al., 2006). The chloride diffusion coefficient of the surface-treated layer is considerably lower than that of the concrete substrate, indicating that the surface treatment could also improve the chloride ion penetration resistance of concrete even with supplementary cementitious materials.

It should be pointed out that these comparisons have two limitations. First, chloride ingress is a complicated process, including diffusion, capillary suction and migration. The current RNA approach just facilitates a rapid prediction of the diffusion process in surface-treated concrete. Second, the time-dependency of the chloride diffusion coefficients is not considered in the comparisons with immersion tests results due to the relatively short exposure period (i.e., 180 days). It is believed that the time-dependency of chloride diffusivity of surface-treated concrete should also depend on the type of hydrophobic material used and needs to be further investigated based on more comprehensive tests in the future.

8. RNA-based Monte Carlo simulation of the probability of corrosion initiation of the reinforced concrete port structure

The probability of corrosion initiation of steel reinforcement in the surface-treated concrete port structure as described in section 7.2 is estimated with RNA-based Monte Carlo simulation. The parameters used for the simulation are summarised in Table 5. The diffusion coefficient of the concrete substrate $D_{t_0,1}$ follows a lognormal distribution with a coefficient of variation (COV) of 0.2 at reference age t_0 according to Val & Trapper (2008). Its mean value is taken as 3.5×10^{-12} m^2/s according to the regression values of D_2 after the 180-day chloride immersion test (Table 4). Due to the lack of experimental data, this paper assumes that the diffusion coefficient of the surface-treated layer also follows a lognormal distribution with a COV of 0.2. Its mean value is taken as $D_{t_0,2}/m$, where m varies from 1 to 30 for the parametric analysis according to the regression results of the saltwater immersion test (Table. 4). m =1 means an untreated concrete. The time-dependency of the concrete substrate is described by a power function of Equation (19) according to Duan et al. (2014), where α_1 follows a normal distribution with a mean value of 0.15 and a COV of 0.2. Because there is little information on the time-dependency of the surface-treated layer, it is assumed in this study that it can be also described by the above-mentioned power function. The power function of Equation (19) represents the degradation of the surface-treated layer when the aging factor α_2 is negative. α_2 is assumed to follow a normal distribution with a COV of 0.2 in this study. The mean value of α_2 varies from −0.1 to −0.5 for the parametric analysis.

Table 5 Parameters for Monte Carlo simulation.

According to the field investigation of the concrete port (Liu & Wang, 2016), the concrete cover depth h_s follows a normal distribution with a mean of 70 mm and a COV of 0.15 (Figure 12a) and the thicknesses of the surface-treated layer h_1 follows a lognormal distribution with a mean of 2.5 mm and a COV of 0.8 (Figure 12b). The initial surface chloride $C_{t_{st}}^{x=0}$ (Equation (23)) follows a lognormal distribution (Vu & Stewart, 2000) with a mean of 2% and a COV of 0.3 (Bentz, 2003). The ultimate surface chloride content $C_u^{x=0}$ follows a lognormal distribution with a mean of 4% (Hackl & Kohler, 2016) and a COV of 0.3 (Duan et al., 2014). The aging factors of the ultimate surface chloride content (i.e. β) and the critical chloride content of corrosion C_{cri} follow the same distributions used by Duan et al. (2014). The reference time of diffusion coefficient t_0 and the initial exposure time t_{st} are assumed to be 28 and 56 days, respectively. All the distributions are checked before calculation, and it will be rebuilt if any of them is not in a proper range.

Figure 13 Field investigation of surface-treated concrete port for (a) beam concrete cover depth (b) liquid silane penetration depth (Liu & Wang, 2016).

It is assumed in this study that the passive layer on the steel bar surface is destroyed when the chloride concentration $C_{h_s}^{cal}$ at concrete cover depth h_s reaches the critical chloride content C_{cri}, leading to the initiation of steel corrosion. Thus, the possibility of corrosion initiation $P_{cr}(T)$ at time T is given by

$$P_{cr}(T) = \Pr[C(h_s, T) \geq C_{cri}] \tag{25}$$

The sample size for the Monte Carlo simulation was set as two million. The convergence analysis showed that such a sample size is large enough to provide a satisfied estimation (Figure. 13). All the calculations were completed in 12 hours by parallel computing on a common laptop computer (CPU Intel i5-8265U, 1.60 GHz).

Figure 14 Effect of sample size on convergence. (M represents million).

Figure 14a illustrates the simulated time-dependent probability of corrosion initiation of steel reinforcement in the surface-treated concrete. It is seen from Figure 14 that the probability increases as the chloride diffusion coefficient of the surface-treated layer increases. The corrosion initiation time of the concrete port ($D_{t_0,1} = D_{t_2,2}/1$) is 10 years when the target probability of corrosion initiation is set as 20%. For surface-treated concrete, however, the initiation time increases to 14 and 18 years when *m* increases to 15 and 30, respectively. This shows that surface-treatments could considerably improve the durability of concrete structures and the diffusion coefficient of the surface-treated layer is an important parameter for enhance the chloride ion penetration resistance of surface-treated concrete structures.

Figure 15 Effects of (a) chloride diffusion coefficient and (b) time-dependency on corrosion probability of steel reinforcement in surface-treated concrete.

Figure 14 illustrates the effect of time-dependency on the probability of corrosion initiation. A common concrete structure ($D_{t_0,1} = D_{t_2,2}/1$) is not sensitive to the degradation parameter α_1 of the first layer. In contrast, the degradation parameter α_1 exhibits a more significant effect on the probability of corrosion initiation, as shown in Figure 14b. The corrosion initiation time is 16 years when the chloride diffusion coefficient of the surface-treated layer is constant (i.e., when α_1 is 0). When α_1 decreases to −0.50, the corrosion initiation time decreases to 11 years. Therefore, the degradation of surface-treated layer plays an important role in the service life of RC structures.

In conclusion, compared with the FEM, the proposed RNA significantly improves the computational efficiency and facilitates the likelihood prediction of time-dependent corrosion initiation of reinforcement. Therefore, this approach has great potential to be applied to the durability assessment and design of surface-treated concrete structures in engineering practice.

9. Conclusions

An RNA has been developed that allows for an accurate prediction of chloride diffusion in bilayer materials. In this approach, the time-dependency has been considered for the chloride diffusion coefficient of each material and for the surface chloride content. The numerical results obtained with the RNA are in very good agreement with those obtained with the FEM for both simple and complicated cases. The RNA greatly improves the computational efficiency and can be used to investigate the progress of chloride diffusion in surface-treated concrete in a quantitative manner. Monte Carlo simulation has been used to estimate the probability of corrosion initiation in RC structures in marine environments. Parametric analyses have been conducted for an actual RC port structure. The results indicate that the performance of surface-treated concrete structures is significantly influenced by the protection effectiveness and time-dependency of chloride diffusion coefficient of the surface-treated layer.

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