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Abstract - A theoretical study is presented on the effect of surface treatments on chloride diffusion in surface-treated concrete. Analytical solutions are derived for chloride diffusion in both the two-layer model and single-layer model with a convective boundary condition. The former consists of the treated surface layer and the substrate layer of concrete; whereas the latter consists of only the substrate layer with the convective boundary representing the effect of the treated thin surface layer on the chloride diffusion in the substrate layer. The analytical solutions are validated using the numerical model and published experimental results. The results show that the effect of surface treatments on the chloride diffusion in the substrate layer of concrete can be represented by using the convective coefficient, expressed in terms of the diffusion coefficient of chlorides in the treated surface layer divided by the thickness of the treated surface layer.

Keywords – Chloride; Diffusion; Surface treatment; Concrete; Modelling.

1. Introduction

Concrete is a porous material in which its pores are filled with water and air. When the concrete is exposed to a marine environment, chlorides that are dissolved in moisture surrounding the concrete can ingress into concrete through the connective pore system of concrete. When the chloride concentration inside the concrete at the place where a reinforcing steel is located reaches to a threshold value the corrosion of the reinforcing steel will start. To prevent the reinforcement from corrosion one has to restrict the penetration of chlorides from environment into concrete. This could be done either by increasing the concrete cover or using surface treatment technology to provide additional barrier on the concrete surface. The former is normally applied for new structures, whereas the latter could be applied for both the new and existing structures. In this paper our focus will be on the surface treatments, in particular addresses the problem - how to quantify the effect of surface treatments on the penetration of chlorides in cementitious materials. The terminology of “surface-treated concrete” used in the present study means that the concrete has a thin layer on its surface which is different from its substrate in terms of its resistance to ionic diffusion. That thin layer could be the coating or the original concrete but with some treatment and thus has higher resistance to ionic diffusion.

Since early of 1990s extensive research has been carried out on the durability of surface treated concrete, particularly in relation to the problem of chloride-induced reinforcing steel corrosion in concrete structures. The work includes the laboratory and site investigations to examine the
effectiveness and protective mechanisms of surface treatments in resisting chloride ingress and the development of theoretical models to understand how a surface treatment can limit chloride diffusion and to predict how chloride is distributed in the surface-treated concrete. For example, Swamy and Tanikawa [1] evaluated the effectiveness of different surface coatings on their ability to control chloride penetration and corresponding reinforcing steel corrosion using accelerated wet-dry and continuous salt spray tests. Jones et al. [2] experimentally examined the influence of various surface treatments on the chloride diffusion properties of concrete. Ibrahim et al. [3] investigated the effectiveness of different materials used in surface treatments in reducing chloride-induced reinforcement corrosion. Basheer et al. [4] reported a study on the performance assessment of surface-treated concrete. Andrade et al. [5] presented a mathematical model to predict the skin effect on the chloride diffusion in surface-treated concrete. Swamy et al. [6] examined the ability of acrylic-based surface coating systems in protecting the penetration of chloride and carbon-dioxide into concrete. Buenfeld’s research team at Imperial College London [7,8,9] investigated the chloride diffusion in surface-treated mortar and concrete specimens by using both experimental and numerical methods. Page’s research team at Aston University [10,11] studied the characteristics and performance of surface coatings applied to concrete for the protection of reinforcing steel from corrosion. Medeiros and Helene [12] carried out a study on the surface treatment of reinforced concrete in marine environment to examine the influence of surface treatments on chloride diffusion coefficient and capillary water absorption. Yoon et al. [13] presented a numerical formulation, based on Nernst–Plank equation, to describe the effect of surface treatments on specimens tested by rapid chloride permeability tests. Pigino et al. [14] investigated the characteristics and performance of the surface-treated concrete when the surface was treated by using ethyl silicate. Sivasankar et al. [15] provided a quantifiable estimation on the procrastinating of reinforcing steel corrosion in surface-treated concrete using sealers. Pritzl et al. [16] examined the influence of using penetrating sealer on chloride ingress in different bridges in Wisconsin. Petcherdchoo [17], Petcherdchoo and Chindaprasirt [18] presented the closed-form solutions for the chloride diffusion in concrete in which the surface chloride concentration was assumed to be time-dependent. A bilinear function and an exponential function were employed respectively in their studies to represent the effect of the applied surface treatment. Recently, Yang et al. [19] investigated the effect of surface treatments on the chloride transport at the cementitious spacer-concrete interface. Geng et al. [20] reported a new concrete hydrophobic treatment method by using SiO\textsubscript{2} sol and silane emulsion. It was found that the hydrophobic effect of the SiO\textsubscript{2} sol and silane emulsion was largely due to the change of the surface morphology of the concrete.

The above literature survey shows that, despite the considerable amount of work published in literature on chloride diffusion in surface-treated concrete, there is very limited work on the development of mathematical models, which are able to describe the direct effect of surface treatments on chloride penetration. Most of existing models were developed based on the use of a few of time-dependent surface chloride concentration functions to reflect the influence of surface treatments [17,18,21]. The relation between the assumed time-dependent surface chloride concentration and the surface treatment parameters was not established, but purely empirical, which limits the application of the models. In this paper a theoretical analysis model is developed for describing chloride ingress in surface-treated concrete. The model starts with the use of two layers; one represents the treated surface layer and the other stands for the substrate layer of concrete. The two layers are assigned to have different diffusion properties. Analytical solution is derived for the chloride diffusion in the two-layer model. When the two-layer model is applied to the case where the treated surface layer is extremely thin, the two-layer model can be simplified into a single-layer model with a convective boundary condition.
representing the effect of the treated thin surface layer on the chloride diffusion in the substrate layer. Analytical solution is also derived for the single layer model with the convective boundary condition.

2. Chloride diffusion in two-layer model

In most existing diffusion models concrete is assumed as a single medium in which its diffusion properties are usually assumed not to change with spatial coordinates. However, when a surface treatment is applied to the concrete, the diffusion properties in the treated surface layer will be different from those in the substrate of the concrete. For the simplicity of presentation, herein, we consider the one-dimensional diffusion problem of chlorides in a surface-treated concrete when it is exposed to a chloride environment. The surface treatments could be the application of coatings or the use of penetrants or sealers [8]. Without loss of generality, the surface-treated concrete can be divided into two layers; one represents the treated surface layer, which could be the coating or the layer where the pore structure of the concrete has been improved, and the other stands for the substrate layer (see Fig. 1). The governing equations controlling the chloride diffusion in the surface-treated concrete thus can be expressed as follows,

For $-\delta < x < 0$ (in treated surface layer)

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left( D_1 \frac{\partial C_1}{\partial x} \right)$$  \hspace{1cm} (1)

For $0 < x$ (in substrate layer)

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} \left( D_2 \frac{\partial C_2}{\partial x} \right)$$  \hspace{1cm} (2)

where $C_1$ and $D_1$ are the concentration and diffusion coefficient of chlorides in the treated surface layer, $C_2$ and $D_2$ are the concentration and diffusion coefficient of chlorides in the substrate layer, $\delta$ is the thickness of the treated surface layer, $t$ is the time, and $x$ is the coordinate with the origin defined at the interface between the two layers. The solution of Eqs. (1) and (2) for $C_1(t, x)$ and $C_2(t, x)$ requires to have the following initial and boundary conditions,

$$C_1(0, x) = C_2(0, x) = 0$$  \hspace{1cm} (3)

$$C_1(t, -\delta) = C_s$$  \hspace{1cm} (4)

$$C_1(t, 0) = C_2(t, 0) = C_0(t)$$  \hspace{1cm} (5)

$$D_1 \frac{\partial C_1(t, 0)}{\partial x} = D_2 \frac{\partial C_2(t, 0)}{\partial x}$$  \hspace{1cm} (6)

$$C_2(t, \infty) = 0$$  \hspace{1cm} (7)

where $C_s$ is the environment concentration of chlorides on the exposed surface which is a constant, and $C_0$ is the concentration of chlorides at the interface between the two layers which is the unknown function of time. Eq. (3) is the initial conditions for $C_1(t, x)$ and $C_2(t, x)$. Eqs. (4) and (7) are the boundary conditions for $C_1(t, x)$ and $C_2(t, x)$. Eqs. (5) and (6) represent the continuous conditions at the interface between the two layers. For given a problem ($C_s$, $\delta$, $D_1$ and $D_2$ are knowns) one can solve Eqs. (1)-(7) for $C_1(t, x)$ and $C_2(t, x)$ numerically from which
the effect of the applied surface treatment (δ, D₁) on the chloride diffusion in the substrate layer of concrete can be evaluated. Such work can be seen, for instance, in refs. [5,8], and thus is not to discuss further. When the surface layer is very thin, a multiscale model or an adaptive scheme may be needed to find the convergent solutions of Eqs.(1)-(7) [22].

According to Carslaw and Jaeger [23] (page 321) and Crank [24] (page 41), however, an analytical solution can also be obtained for Eqs. (1)-(7), which is expressed as follows,

\[ C_1(t, x) = C_s \sum_{n=0}^{\infty} \alpha^n \left( \text{erfc} \left( \frac{(2n+1)\delta+x}{2\sqrt{D_1 t}} \right) \right. \]

\[ \left. - \alpha \text{erfc} \left( \frac{(2n+1)\delta-x}{2\sqrt{D_1 t}} \right) \right) \]

\[ C_2(t, x) = \frac{2kC_s}{k+1} \sum_{n=0}^{\infty} \alpha^n \text{erfc} \left( \frac{(2n+1)\delta+kx}{2\sqrt{D_1 t}} \right) \]

where \( k = \sqrt{D_1/D_2} \) and \( \alpha = \frac{1-k}{1+k} \) are the dimensionless constants, and \( \text{erfc}(.) \) is the complementary error function. The use of an analytical solution, instead of the numerical solution, is more convenient to examine the effect of the surface treatments on the chloride diffusion in the substrate layer. The examination of Eq. (9) indicates that, if \( k \to 1 \) and \( \delta \to 0 \), then \( C_2(t, x) \) given by Eq. (9) reduces to the well-known error function solution of Fick’s second law. The concentration at the interface (\( x=0 \)) thus can be obtained from either Eq. (8) or (9) as follows,

\[ C_o(t) = C_1(t, 0) = C_2(t, 0) = \frac{2kC_s}{k+1} \sum_{n=0}^{\infty} \alpha^n \text{erfc} \left( \frac{2n+1}\sqrt{D_1 t} \right) \]

It is obvious that if \( k \to 1 \) and \( \delta \to 0 \), then \( C_o(t) \to C_s \). Eqs. (9) and (10) thus directly reflect the effect of the surface treatment on the chloride diffusion in the substrate layer of concrete. It can be seen from Eq. (10) that the concentration at the interface decreases with the increase of \( \delta \) or the decrease of \( k \). As an example, Fig. 2 shows the comparisons between the numerical solution obtained by using finite difference method to solve Eqs. (1)-(7) and the analytical solution of Eqs. (8)-(10) for the chloride distribution profiles at three different times and the time-history of chloride concentration at the interface (\( x=0 \)). The scheme employed for obtaining the numerical solution of Eqs. (1)-(7) can be found elsewhere, for instance, in Refs. [25,26,27] and thus is not further explained herein. The comparison shown in the figure demonstrates that the series involved in Eqs. (8)-(10) have very good convergence as the analytical solutions shown in the figure use only first two terms of the series. Fig. 3 shows the individual effects of \( D_1/D_2 \) and \( \delta \) on the chloride concentration at the interface. It can be seen from the figure that the increase of the thickness of the treated surface layer leads to a proportional decrease of the chloride concentration at the interface. In contrast, the decrease of diffusion coefficient in the treated surface layer can more effectively decrease the chloride concentration at the interface. Both figures in Fig. 3 show that the chloride concentration at the interface increases initially quickly, but with the increase of time it tends to be stabilized and gradually approach to its up-limit value which is close to the environment chloride concentration \( C_s \).

3. Chloride diffusion in substrate with convective boundary condition

The analytical solution described in the above section can be used to examine the effect of the surface treatments on chloride diffusion in the substrate layer of concrete. However, the form of the solution has some shortcomings. Firstly, the solution is expressed by the series which is not very convenient to use. Secondly, the effect of the surface treatments on the chloride
diffusion in the substrate layer is represented by the thickness of the treated surface layer and the diffusion coefficient of chlorides in the treated surface layer, both of which are difficult to determine. Note that, in most surface-treated concrete the thickness of the treated surface layer is very thin. Thus, the concentration gradient of chlorides in the treated surface layer can be approximately expressed as follows,

$$\frac{\partial C_1(t,0)}{\partial x} = \frac{C_o-C_s}{\delta}$$  \hspace{1cm} (11)

In this case, the boundary condition given by Eq.(6) can be simplified as follows,

$$D_2 \frac{\partial C_2(t,0)}{\partial x} = D_1 \frac{\partial C_1(t,0)}{\partial x} = \frac{D_1}{\delta} [C_o(t) - C_s] = h_s [C_2(t,0) - C_s]$$ \hspace{1cm} (12)

where \( h_s = D_1/\delta \) is a parameter that is similar to the convective coefficient used in the heat transfer, and thus, herein, is referred to as the convective coefficient of ionic diffusion [28]. The solution of the diffusion equation defined by Eq. (2) for the substrate layer with the initial condition defined by Eq. (3), and boundary conditions defined by Eqs. (12) and (7) can be expressed as follows [24] (page 36),

$$C_2(t,x) = C_s \text{erfc} \left( \frac{x}{2\sqrt{D_2 t}} \right) - C_s \exp \left( \frac{h_s x + h_s^2 t}{D_2} \right) \text{erfc} \left( \frac{x + 2h_s t}{2\sqrt{D_2 t}} \right)$$ \hspace{1cm} (13)

Mathematically, the first term in the right-hand-side of Eq. (13) represents the diffusion profile when the actual surface chloride concentration is the same as the environment chloride concentration, that is \( C_o = C_s \), whereas the second one represents the effect of the treated surface layer on the chloride profile in the substrate layer, which is generated due to the use of the convective boundary condition. The examination of Eq. (13) indicates that, if \( h_s \to \infty \), then the second term in Eq. (13) tends to zero and thus \( C_2(t,x) \) reduces to the well-known error function solution of Fick’s second law. To demonstrate the analytical solution of Eq. (13), Fig. 4 shows a comparison between the numerical solution obtained by using finite difference method to solve Eqs. (1)-(7) and the analytical solution of Eq. (13) for the chloride distribution profiles in the substrate layer at three different times. Note that Eq. (13) is only for the substrate layer. It can be seen from the figure that even for a thick treated surface layer \( (\delta=5 \text{ mm}) \), the analytical solution is still quite accurate, particularly when the time becomes large.

The chloride concentration at the interface can be obtained by letting \( x=0 \) in Eq. (13), which can be expressed as follows,

$$C_o(t) = C_s \left[ 1 - \exp \left( \frac{h_s^2 t}{D_2} \right) \text{erfc} \left( \frac{h_s t}{\sqrt{D_2 t}} \right) \right]$$ \hspace{1cm} (14)

Note that,

$$\exp(z^2)\text{erfc}(z) = \frac{1}{\sqrt{\pi}} \left( \frac{1}{z} - \frac{1}{2z^3} + \frac{1}{2^3z^5} + \cdots \right)$$ \hspace{1cm} (15)

Thus, if \( h_s \to \infty \) then \( C_o(t) \to C_s \), which represents the case where the surface chloride concentration is constant. Eq. (14) indicates that the variation of the chloride concentration at the interface, which is obtained by considering the influence of the treated surface layer represented by the convective boundary condition, is dependent on a single parameter \( (h_s^2 t/D_2) \)
and is controlled by the multiplication of an exponential function and a complementary error functions. Fig. 5 graphically shows the variation of the chloride concentration at the interface with the parameter \((h_c^2/D_2)\). This variation can be approximated using a power function, which is also superimposed in the figure. The influence of the convective coefficient on the time-history of the chloride concentration at the interface can be interpreted as a scale factor to the time. It is noted from Eqs. (13) and (14) that, the chloride diffusion in a surface-treated concrete depends on the environment chloride concentration \((C_v)\), the convective coefficient \((h_c)\) representing the effect of the treated surface layer, and the diffusion coefficient of chloride \((D_2)\) in the substrate layer of concrete. Finally, to demonstrate the present analytical solution of Eq. (13), Fig. 6 shows a comparison of the chloride concentration profiles calculated from Eq. (13) and those measured in experiments [18,29]. In the experiments [29] the concrete was mixed with water (200 kg/m³), cement (400 kg/m³), fine aggregate (778 kg/m³), and coarse aggregate (956 kg/m³). After having a standard curing the concrete prism specimens were sealed using epoxy polyurethane on the five surfaces and the remaining surface was treated using two cementitious coatings (each 1.0 kg/m²) for examining the effect of the coating surface treatment on chloride diffusion in the specimens. After they were immersed in the seawater for the periods of 9, 36 and 60 months, the specimens were then taken to laboratory for determining the chloride concentration profiles. In the analytical solution the parametric values for the environment chloride concentration, convective coefficient, and diffusion coefficient of chloride in the substrate layer are taken as \(C_v=2\%\) wt. of concrete, \(h_c=1.4\times10^{-10}\) m/s, and \(D_2=3.5\times10^{-12}\) m²/s, respectively. It can be seen from the figure that there is reasonably good agreement between the analytical solution and the experimental data. The slight division for the profile at 36 months is probably due to the random weather conditions happened in the tests. Note that if a artificial time-varying surface chloride concentration were employed a time-dependent diffusion coefficient would also have to be used in order to match the test data [18], whereas the diffusion coefficient employed in the present study is a constant, not time-dependent. Note that, the use of the convective boundary condition is mathematically different from the use of time-varying surface chloride concentration, although the former also leads to the surface chloride concentration which varies with time.

Surface chloride concentration is an important parameter in predicting the durability and service life of concrete structures [30,31]. The surface treatment of concrete can protect the substrate concrete from the exposed environment and lead to low chloride concentration in inner side of the concrete [32,33]. Surface treatments are very effective to improve the durability of concrete structures and to deaccelerate the penetration of chloride from the surrounding environment into concrete. Various surface treatment technologies have been applied practically, for example, in bridges [34,35,36,37].

### 4. Conclusions

In this paper, we have presented a theoretical study on the effect of the surface treatments on the chloride diffusion in surface-treated concrete. Analytical solutions have been developed for the chloride diffusion in the two-layer model and in the single-layer model with the use of a convective boundary condition representing the effect of the treated thin surface layer on the chloride diffusion in the substrate layer of concrete. The analytical solutions have also been validated using the numerical model and experimental results from site tests published in literature. From the results obtained, the following conclusions can be drawn.

- The effect of the surface treatments on the chloride diffusion in surface-treated concrete can be generally examined by using a two-zone model; on represents the treated surface
layer and the other stands for the substrate layer of concrete. Analytical solutions of series form are achieved for the diffusion profiles of chlorides in the two zones, which reflects the effect of the diffusion coefficients of chlorides in the two zones and the thickness of the treated surface layer.

- When the thickness of the treated surface layer is very thin the chloride diffusion problem in the surface-treated concrete can be approximately modelled as the chloride diffusion problem in the substrate layer of concrete alone but with the use of a convective boundary condition. In other words, the two-zone model can be simplified into a single-zone model for the substrate layer but with a convective boundary condition. The convective coefficient for ionic diffusion can be expressed in terms of the diffusion coefficient of chlorides in the treated surface layer divided by the thickness of the treated surface layer.

- Owing to the effect of the convective boundary condition, the chloride concentration at the front of the substrate layer (i.e., the interface between the treated surface layer and substrate layer) increases with time but will be always smaller than the chloride concentration in the environment. The relationship between these two concentrations can be described by a unified parameter \( (h c t / D c) \) and is expressed by Eq. (14).

- Analytical solution in the single-zone model with the use of convective boundary condition is also achieved for the diffusion profile of chlorides in the substrate layer, which is expressed by the combination of the exponential function and error function. The effect of the treated surface layer on the chloride diffusion in the substrate layer is directly reflected by the convective coefficient involved in the exponential and error functions.

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**References**

Figure 1. Schematic of chloride diffusion in surface-treated concrete.
Figure 2. Comparison between analytical and numerical solutions (a) for chloride concentration distribution profiles at three different times and (b) for the chloride concentration at the interface ($D_2=1.0\times10^{-11} \text{ m}^2/\text{s}$, $D_f=0.5D_2$, $\delta=10 \text{ mm}$).
Figure 3. Effect of surface treatments on chloride concentration at the interface (a) $D_2=1.0 \times 10^{-11}$ m$^2$/s and $D_1=0.5D_2$ and (b) $D_2=1.0 \times 10^{-11}$ m$^2$/s and $\delta=2.5$ mm.

Figure 4. Comparison between analytical and numerical solutions for chloride concentration distribution profiles at three different times ($D_2=1.0 \times 10^{-11}$ m$^2$/s, $D_1=0.5D_2$, $\delta=5$ mm).
Figure 5. Variation of chloride concentration at interface with dimensionless time.

Figure 6. Comparison between analytical solution and test data [29] (Parametric values used in analytical solution are $C_s=2.0\%$ wt. of concrete, $h_s=1.4 \times 10^{-10}$ m/s, $D_2=3.5 \times 10^{-12}$ m$^2$/s).