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## Analytical solution and experimental validation for dual time-dependent chloride diffusion in concrete

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### HIGHLIGHTS

- A new analytical solution was developed for dual time-dependent chloride diffusion in concrete.
- Influences of time-dependent behaviour of  $D$  and  $C_s$  were investigated.
- The proposed solution is applicable for various time-dependent models of surface chloride concentration with high accuracy.

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### ABSTRACT

An analytical solution for dual time-dependent chloride diffusion within concrete was developed by taking into account the time-dependent behaviour of both surface chloride concentration and chloride diffusion coefficient. Firstly, the time-varying chloride diffusion coefficient was transformed into a constant one by introducing the equivalent diffusion time. Then an analytical solution for dual time-dependent chloride diffusion within concrete was presented based on the Duhamel's theorem. Finally, the accuracy and applicability of the proposed analytical solution were validated by comparing with field data, existing approximate analytical solutions and numerical results from finite element analysis. Analysis results show that the influence of time-dependent behaviour of chloride diffusion coefficient on the chloride concentration distribution within concrete is much larger than that of surface chloride concentration. Furthermore, the proposed solution is applicable for various kinds of (such as square-root, exponential, logarithmic and power-law, etc.) time-varying models of surface chloride concentration with high accuracy.

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### 1. Introduction

It has been widely recognized that chloride diffusion coefficient and surface chloride concentration of concrete are two important parameters for describing the diffusion process and concentration distribution of chloride ion within concrete. During the early period, the analytical solution for the Fick's second law of diffusion has been proposed by taking both the chloride diffusion coefficient and surface chloride concentration as constants [1], which is referred to as the analytical solution with dual constant parameters (ASDC). The ASDC is simple to implement and has been widely used in service life prediction [2,3] and durability analysis [4–6] of

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concrete structures. However, it was observed that the chloride diffusion coefficient usually decreases with the exposure period of concrete structure due to the hydration process of cement paste [7–9]. Based on this phenomenon, Mangat and Molloy [8], Maage et al. [9], DuraCrete [10] and Tang et al. [11] proposed several types of analytical solutions for chloride diffusion with time-varying chloride diffusion coefficient. However, above solutions ignore the time-dependent behaviour of surface chloride concentration of concrete ( $C_s$ ). Due to the influences of material properties and environmental conditions of concrete structure,  $C_s$  also exhibits obvious time-dependent behaviour. Several types of time-varying models including linear [12,13], square root [13,14], power-law [15], logarithmic [16,17] and exponential [18] functions have been adopted to describe the time-dependent behaviour of surface chloride concentration. Moreover, Kassir et al. [18] proposed an analytical solution for chlorine diffusion in concrete with time-varying

surface chloride concentration, but it ignores the time-dependent behaviour of chloride diffusion coefficient.

As discussed above, the chloride diffusion coefficient often decreases, while the surface chloride concentration of concrete usually increases, with the increasing exposure period of concrete structure [13,14,16,17]. Therefore, it is necessary to develop an analytical solution for the dual time-dependent diffusion of chloride within concrete by taking into account the time-dependent behaviour of both chloride diffusion coefficient and surface chloride concentration. Costa et al. [15] proposed an approximate analytical solution for the dual time-dependent chloride diffusion within concrete by replacing the constant chloride diffusion coefficient and constant surface chloride concentration in the ASDC with time-varying ones. Petcherdchoo et al. [14] and Pack et al. [16] developed another kind of approximate analytical solution for the dual time-dependent chloride diffusion problems by replacing the constant diffusion coefficient with the time-varying one in the analytical solution of chloride diffusion model with time-varying surface chloride concentration. However, the accuracy of the above approximate analytical solutions might be questionable, since they ignore the coupling effects of time-dependent behaviour between chloride diffusion coefficient and surface chloride concentration of concrete. Hence, it is desirable to develop an efficient and accurate analytical solution for dual time-dependent chloride diffusion within concrete.

The main objective of this study is to develop an analytical solution for the dual time-dependent chloride diffusion within concrete by taking into account the time-dependent behaviour of both surface chloride concentration and chloride diffusion coefficient of concrete. The time-varying chloride diffusion coefficient was converted into a constant one by introducing the equivalent diffusion time. Then an analytical dual time-dependent solution for chloride diffusion within concrete was developed based on the Duhamel's theorem. Finally, the accuracy and applicability of the proposed analytical solution were validated by comparing with existing approximate analytical solutions, numerical results of finite element analysis and field data. Furthermore, the influences of time-dependent behaviour of chloride diffusion coefficient and surface chloride concentration of concrete on the diffusion process and concentration distribution of chloride ions within concrete were also investigated.

## 2. Analytical solution for dual time-dependent chloride diffusion

In order to take into account the time-dependent behaviour of both chloride diffusion coefficient and surface chloride concentration of concrete, it was assumed that the chloride diffusion coefficients along three orthogonal directions are all equal to  $D(t)$  and the chloride concentrations on the three orthogonal concrete surfaces are all equal to  $C_s(t)$ . Based on the above assumption, the governing equation of chloride diffusion within concrete can be expressed by the Fick's second law of diffusion as [19]

$$\frac{\partial C(\mathbf{x}, t)}{\partial t} = D(t) \nabla^2 C(\mathbf{x}, t); \mathbf{x} \in \Omega \quad (1)$$

where  $C(\mathbf{x}, t)$  is the chloride concentration at point  $\mathbf{x}$  and exposure time  $t$  (% by weight of binder);  $\mathbf{x}$  is the spatial coordinate within concrete. For one-, two- and three-dimensional diffusion problems,  $\mathbf{x} = [x_1]$ ,  $\mathbf{x} = [x_1, x_2]^T$  and  $\mathbf{x} = [x_1, x_2, x_3]^T$  respectively, where  $x_1$ ,  $x_2$  and  $x_3$  are the distances from the point to concrete surfaces along different coordinate axes;  $D(t)$  is the time-dependent chloride diffusion coefficient;  $\nabla^2$  is the Laplace operator;  $\Omega$  denotes the domain of chloride diffusion.

The boundary conditions and initial conditions of Eq. (1) are defined as follows [19]

$$C(\mathbf{x}, t)|_{\mathbf{x} \in \Gamma} = C_s(t); C(\infty, t) = C_0; C(\mathbf{x}, 0) = C_0 \quad (2)$$

where  $C_s(t)$  is the surface chloride concentration (% by weight of binder), which is a function about exposure time  $t$ ;  $\Gamma$  denotes the boundary of the concrete exposed to chloride environment;  $C_0$  is the initial chloride concentration within concrete (% by weight of binder).

According to reference [11], the time-varying chloride diffusion coefficient  $D(t)$  can be described as

$$D(t) = D_{\text{ref}} \left( \frac{t_{\text{ref}}}{t'} \right)^n \quad (3)$$

where  $t'$  is age of concrete (a);  $D_{\text{ref}}$  is chloride diffusion coefficient at reference time  $t_{\text{ref}}$  ( $\text{mm}^2/\text{a}$ ).

If the age of concrete initially exposed to chloride environment  $t_0$  is equal to the reference age  $t_{\text{ref}}$ , then  $t' = t + t_0$  and  $D_{\text{ref}} = D_0$ , Eq. (3) can be rewritten as

$$D(t) = D_0 \left( \frac{t_0}{t + t_0} \right)^n = D_0 f(t) \quad (4)$$

$$f(t) = \left( \frac{t_0}{t + t_0} \right)^n \quad (5)$$

where  $t_0$  is the age of concrete initially exposed to chloride environment (a);  $D_0$  is usually called the initial diffusion coefficient ( $\text{mm}^2/\text{a}$ ), which is usually related to factors such as concrete type, water-to-cement ratio and mineral admixtures [14,15]. Meanwhile, the influence of temperature variations on the chloride diffusion within concrete can further be considered by introducing the temperature correction factor [20,21] into the definition of chloride diffusion coefficient  $D(t)$ .  $n$  is the aging factor, which is regarded as a parameter associates with the amount of fly ash and slag replacement and can be determined by [22,23]:

$$n = 0.2 + 0.4 \times \left( \frac{R_{\text{FA}}}{0.50} + \frac{R_{\text{SG}}}{0.70} \right) \quad (6)$$

where  $R_{\text{FA}}$  is the amount of fly ash replacement (% by weight of binder);  $R_{\text{SG}}$  is the amount of slag replacement (% by weight of binder).

It has been observed that chloride diffusion coefficient often decreases while the surface chloride concentration of concrete usually increases with the increasing exposure period of concrete structures [13,14,16,17]. The piecewise functions were sometimes adopted to describe the time-dependent behaviour of chloride diffusion coefficient [10,12] and surface chloride concentration [3,12], which means that the chloride diffusion coefficient and the surface chloride concentration vary with exposure time during the early exposure period (e.g., the first 10–30 years), and then turn abruptly to be a constant. However, the chloride diffusion coefficient and surface chloride concentration should change gradually with increasing exposure time. Furthermore, it is quite difficult to analytically solve the time-dependent chloride diffusion equation with piecewise type of chloride diffusion coefficient and surface chloride concentration. Hence, the continuous type function as defined by Eq. (4) was adopted to describe the time-dependent behaviour of chloride diffusion coefficient in this study. According to Eq. (4), the aging factor  $n$  represents the degradation rate of chloride diffusion coefficient. Without loss of generality, taking  $t_0 = 28$  d and  $D_0 = 3.0 \times 10^{-12} \text{ m}^2/\text{s} = 94.61 \text{ mm}^2/\text{a}$  as an example here, the influence of aging factor on the time-dependent behaviour of chloride diffusion coefficient is shown in Fig. 1a. It shows that the chloride diffusion coefficient decreases obviously during the first 20 years and then tends to be stable gradually. It also shows that the larger the aging factor is, the faster the chloride diffusion coefficient

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