



A study of the factors affecting the surface chloride maximum phenomenon in submerged concrete samples

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ABSTRACT

The chloride content analysis of the concrete exposed to chlorides often shows an initial increase in the concentration of chlorides to a maximum point within the first layers from the concrete surface, followed by a gradual reduction in the concentration of chlorides at the lower depths. A review of literature shows that very little attention has been given to the depth (Δx) at which the maximum chloride concentration (C_{\max}) occurs and its potential impacts on the numerical estimation of the apparent chloride diffusion coefficient (D_a) and surface chloride concentration (C_s). This paper studies the influence of water-to-cement ratio (w/c), the concentration of chlorides in the environment, the time-to-exposure, and exposure duration on C_{\max} and Δx . Results show that w/c does not have a significant influence on C_{\max} . However, a significant increase in Δx is observed with an increase in the w/c . Results also show that while C_{\max} has time-variant properties and it increases nonlinearly with the exposure duration, exposure duration has minimal impacts on Δx . In addition, the time-to-exposure and the concentration of chlorides in the exposure environment are found to be significant factors influencing both C_{\max} and Δx . The findings of this study show that Δx has a significant impact on the numerical estimation of D_a and C_s . Because Δx is not limited to the first millimeter of the concrete surface, as specified in ASTM C1556, care must be taken to exclude the layers that correspond to Δx .

1. Introduction

Chloride-induced corrosion of the reinforcing steel in concrete is one of the significant causes of deterioration in the reinforced concrete (RC) structures. Corrosion can lead to cracks in the concrete and cross-sectional loss of the reinforcing steel which in turn can lead to the reduced mechanical strength and shortening the service life of RC structures. External chlorides from the environment (i.e., sea water, deicing, and anti-icing salts) can enter the hardened concrete through different transport mechanisms (i.e., convection, diffusion, electrical migration, and ionic movement due to interactions between ions). In the case of submerged structures in the marine environments, diffusion can be assumed to be the primary transport mechanism. However, when RC structures are subjected to wet and dry cycles (e.g., tidal zone and atmospheric zone), the transport of chlorides into the hardened concrete becomes more complex. In such cases, a combination of several transport mechanisms such as diffusion due to chloride concentration gradient, capillary suction, and convective flow with the flowing water can be the driving force behind the chloride ingress [1–3]. Once chlorides reach the surface of the reinforcing steel in sufficient quantities known

as critical chloride threshold C_T , corrosion can initiate [4]. Accordingly, the time required for corrosion to initiate is referred to as the corrosion initiation period. The service life of a concrete structure is then defined as the initiation time plus the propagation time that is the time required for the corrosion damage to go beyond the acceptable limits specified by the code of practice [1]. Because quantifying the propagation period depends on many variables, in some literature, to simplify the modeling process, the initiation time is used to represent the service life of the structure. To increase the service life of a concrete structure that is exposed to chlorides, performing a routine condition assessment of the concrete cover and reinforcing steel is essential. During the condition assessment, concrete cores are often taken from different parts of the structure and are used to first, determine the concentration of the chlorides at the depth of the reinforcing steel bars, and second, determine the rate of chloride ingress into the concrete. The obtained information is then fed into mathematical models that are used to mimic the transport of chlorides in the concrete to determine the remaining service life of the structure [5].

Regardless of the mathematical model used to simulate the transport of chlorides into concrete, solving the partial differential equations

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that govern the transport mechanisms (e.g., heat transfer and moisture transfer) involves solving a boundary value problem [6]. One of the critical boundary conditions that can significantly affect the service life of RC structures is the concentration of chlorides at the surface of concrete, C_s [7]. For example, Shakouri et al. [8] reported that a 20% reduction in the C_s value can increase the time to corrosion initiation and extend the service life of a structure by 60%, holding other variables constant.

There are several challenges in determining the C_s value. First, C_s is often found numerically by fitting the lab or field measurements to the closed form solution to Fick's second law of diffusion given in Eq. (1),

$$C(x, t) = C_s - (C_s - C_i) \operatorname{erf}\left(\frac{x}{\sqrt{4D_a t}}\right) \quad (1)$$

where $C(x, t)$ is the concentration of chloride (% weight of concrete, cement, or cementitious materials) at time t (sec) and depth of x (m) from the exposed surface. C_i is the initial background chloride (% weight of concrete, cement, or cementitious materials) and erf is the error function. It is important to note Eq. (1) is derived for non-steady-state conditions and by assuming that concrete is a semi-finite medium, with constant C_s and apparent diffusion coefficient D_a . To determine C_s and D_a , an initial value is first guessed for the C_s and this value is changed iteratively using the method of nonlinear least squares until a stopping rule is satisfied (i.e., the sum of square errors between the observed chloride content values and the estimated chloride contents values using Eq. (1) is less than a specified threshold). ASTM C1556 “Standard Test Method for Determining the Apparent Chloride Diffusion Coefficient of Cementitious Mixtures by Bulk Diffusion” [9] that is commonly adopted for determining D_a and C_s [9] does not specify a stopping rule. While different algorithms can be used to solve a nonlinear least squares problem [10], specifying a very small stopping rule in these algorithms may result in non-convergence and using a relatively large stopping rule can either overestimate or underestimate the C_s and D_a values. Therefore, to obtain a reliable estimate of C_s and D_a , there is a need to specify a standard stopping rule for the nonlinear least square method.

Recent findings show that C_s can be time-variant [11–20]. However, there is no consensus on the shape of the time-variant C_s function. While some researchers proposed that C_s can increase linearly with time [16], other researcher reported that C_s can increase nonlinearly with time [14,18,19,21] or considered an asymptote for C_s [13,17,20]. Because Eq. (1) is derived by assuming a constant C_s , a time-variant C_s function cannot be fed into Eq. (1) directly. Therefore, to account for the time dependency of C_s , Fick's second law should be solved with new boundary conditions [14,15,17–20]. One challenge with solving Fick's second law of diffusion using a time-variant C_s function is that the derived closed-form solution, if exists any, can be very complex [15,22] and therefore, researchers are better off solving the transport problem using an advanced numerical method such as finite element or finite difference analysis.

Another challenge in determining C_s is that when Eq. (1) is fitted to a chloride profile obtained either in cores taken from real structures or specimens tested in a laboratory, the chloride content first climbs to a maximum point (hereafter referred to as C_{\max}), at a certain distance, Δx , from the surface, and then reduces at the lower depths [23–26]. Fig. 1 shows a typical chloride profile of a concrete specimen that exhibits such behavior. This phenomenon that is often referred to in the literature as “maximum phenomenon” can be attributed to several reasons [23,24,27]: first, chlorides can be washed out of the concrete surface by rain or other forms of precipitation [23,28]; second, chlorides can move in the outer layer of concrete by convection and not necessarily by diffusion; third, decomposition of chloro-aluminates due to carbonation which in turn can release the bound chlorides into the pore solution; and fourth, dissimilar composition of the outer layer of the concrete from the bulk of concrete.

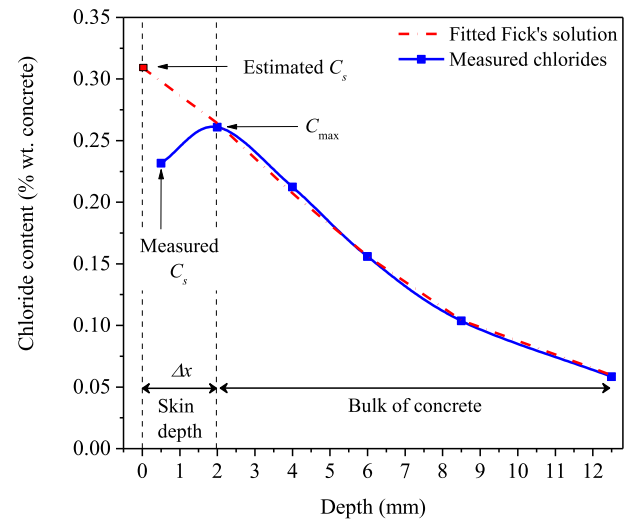


Fig. 1. A typical plot of chloride profile of a concrete specimen.

To account for the differences in the composition of the outer layer than the bulk of concrete, Andrade et al. [23] used the solution to Fick's second law for two-layered interfaces proposed by Crank [29]. The proposed solution assumes that the diffusion coefficient D_1 within the skin depth is different from the diffusion coefficient D_2 in the bulk of concrete.

Assuming the initial conditions of $C_1(x, t) = 0$ for $0 < x < \Delta x$, $C_2(x, t) = 0$ for $x > \Delta x$, and the boundary conditions of $C_1(\Delta x, t) = C_2(\Delta x, t) = 0$ for $t \geq 0$ and $C_1(0, t) = C_s$, the two-layered solution to Fick's second law can be expressed as:

$$C_1(x, t) = C_s \sum_{n=0}^{\infty} \alpha^n \left(\operatorname{erfc} \left[\frac{2n\Delta x + x}{2\sqrt{D_1 t}} \right] - \alpha \operatorname{erfc} \left[\frac{(2n+2)\Delta x - x}{2\sqrt{D_1 t}} \right] \right) \quad (2)$$

$$C_2(x, t) = \frac{2kC_s}{k+1} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left[\frac{(2n+1)\Delta x + k(x - \Delta x)}{2\sqrt{D_1 t}} \right] \quad (3)$$

where $C_1(x, t)$ and $C_2(x, t)$ are the concentration of chlorides in the skin and bulk of concrete, respectively. erfc in Eqs 2. and 3 is the complement error function, $k = \sqrt{\frac{D_1}{D_2}}$, $\alpha = \frac{1-k}{1+k}$, and n is an empirical factor. If the amount of accumulated chlorides due to the resistance between the two zones is expressed as R , the boundary conditions can be rewritten as $C_1(0, t) = C_s$ for $t \geq 0$, and $C_1(\Delta x, t) = R C_2(\Delta x, t)$ for $t \geq 0$. Using these new boundary conditions yields the following solution for C_2 :

$$C_2(x, t) = \frac{2kC_s R}{K+1} \sum_{n=0}^{\infty} \alpha^n \operatorname{erfc} \left[\frac{(2n+1)\Delta x + k(x - \Delta x)}{2\sqrt{D_1 t}} \right] \quad (4)$$

Fig. 1 shows that the increasing trend of chloride concentration within the skin depth Δx is the opposite of the expected trend in a diffusion-type transport mechanism where chlorides move from a higher concentration to the lower concentration. Therefore, Andrade et al. [24] concluded that within the skin depth, a more complex transport mechanism is involved, and therefore, Eqs. (2) and (4) cannot be used when the maximum phenomenon occurs. To determine D_a and C_s , when a chloride profile shows the maximum phenomenon, Andrade et al. [24] proposed rescaling the abscissa of the chloride profile by setting the depth of Δx to zero and fitting Eq. (1) to the rescaled profile.

To better understand the properties of the concrete skin, Sadowski and Stefaniuk [30] studied the microstructural properties of the concrete specimens under four different surface treatments, namely: raw surface, surface in contact with formwork, ground and shot blasted surfaces. Although Sadowski and Stefaniuk [30] did not study the effects of these four surface conditions on C_s , they found that on average,

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