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# Closed-form solutions for modeling chloride transport in unsaturated concrete under wet-dry cycles of chloride attack

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- Closed-form solutions for chloride transport in unsaturated concrete are developed.
- Linearly cyclic surface chloride function for chloride ion modeling is proposed.
- Chloride content is very sensitive to cumulative surface chloride increase.
- Concrete under chloride attack combined with compressive loading is modelled.
- The increase of cyclic chloride attack in some case is found to the power of two.

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#### ABSTRACT

This study proposes a set of new closed-form solutions for a linearly cyclic surface chloride function for predicting the transport of chloride ions in unsaturated concrete. The proposed solutions are validated, and their generality is also tested. From the study, the constant surface chloride calculated by the existing simple closed-form solution is found to be an average of the linearly cyclic surface chloride proposed in this study. Their diffusion coefficient is consistent despite using different closed-form solutions. The chloride content in unsaturated concrete is very sensitive to the time-dependent surface chloride which is cumulatively imposed. The proposed solutions are further applied to concrete with combined actions of chloride attack and compressive loading. A bilinear model for each parameter in the proposed solutions is developed. Apparently, the initial attack and the time-dependent attack of chloride ions is higher, if the stress level is higher than 41% and 19.9%, respectively. Moreover, the resistance of concrete to chloride ions is lower, if the stress level is higher than 29%. In some example, the increase of the surface chloride ions in surface chloride tends to be to the power of two, this is expected to be the reason of faster deterioration of unsaturated concrete.

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#### 1. Introduction

The resistance of concrete to aggressive agents, such as chlorides, sulphates, etc., plays an important role in the durability problem. Various kinds of physical-chemical mechanisms (e.g., diffusion, permeation, and capillary action) governed the transport processes of those aggressive agents which penetrated through the complex microstructures of concrete [1]. For saturated concrete, chloride ions would mainly transport by the diffusion due to concentration gradient [2]. Regarding the diffusion, most of the standard tests relied on concrete being saturated, and the service life prediction of reinforced concrete was designated by using saturated models. However, various experimental studies and analysis provided evidences that concrete would remain unsaturated during construction and throughout its long lifetimes [1,3,4]. In particular, concrete in the tidal, splash and atmospheric zone of off-shore structures as well as concrete subjected to deicing salts was continuously exposed to cycles of capillary uptake and evaporation [5]. On the other hand, the capillary uptake would cause the absorption of salty water containing chlorides into the originally dried concrete [2]. After evaporation, the salt in the absorbed water was however not eliminated from the concrete. And, this remaining salt might cause the accumulation of chloride ions [6]. Šavija et al. [7] stated that chlorides transported by means of several combined mechanisms in unsaturated concrete. And, the unsaturated concrete was of a complicated issue and importance in research. Wu et al. [8] stated that in drying-wetting cycles, the chloride content was caused by not only the concentration gradients, but also the water evaporation and wetting process. Moreover, these drying-wetting cycles could result in the increase in







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the depth of chloride ion penetration. Furthermore, Lu et al. [9] stated that the tidal and splash zone suffering from seawater dryingwetting cycles was the most vulnerable area in terms of steel corrosion in concrete. In particular, the presence of chlorides was linked to a particularly aggressive form of corrosion known as pitting corrosion [10]. The severity of the pitting increased logarithmically with an increase in the concentration of chlorides present in the pore solution [11]. As a result, it is of interest to assess the wet-dry cycle of chloride transport in unsaturated concrete, in particular, the assessment of concrete infrastructure service life [12].

Several researchers have proposed models to predict the transport of chloride ions in unsaturated concrete. For example, Meijers et al. [13] presented computational results of models, which took into account environmental temperature and humidity fluctuations, chloride binding, diffusion and convection, as well as carbonation effects. They stated that the skin layer of concrete in contact with air exhibited a continuously alternating moisture content. Only behind the skin, the moisture content appeared to be constant or slowly alternating, and the chloride diffusion model could be considered. The thickness of the outer layer with fluctuating moisture content was found to depend on the climate, the elevation from the sea water level, and the quality of concrete. This thickness can be treated as the depth of convection zone, as stated in the following statements. Farahani et al. [14] collected data and developed a prediction model of chloride diffusion coefficient for silica fume concrete under long-term exposure to a durability site located in the southern region of Iran. They stated that concrete specimens are saturated below the outer convection zone of the cover in chloride profiles. Yu et al. [15] proposed a chloride diffusion coefficient model coupled with environmental factors to describe chloride ingress into concrete. The S-curve model was also presented to fit the error function. And also, field test and artificial simulated environment experiments were conducted. They showed that the chloride diffusion in concrete could be described by an equivalent chloride diffusion coefficient model, and the measured data of chloride content in concrete corresponded with the fitted profiles. Moreover, under natural and artificial simulated environments, the differences of chloride ingress into concrete could be treated in terms of surface chloride content, convective zone depth, and diffusion coefficient. Costa et al. [16] gathered the chloride concentration profiles obtained experimentally from control samples of an offshore platform after 25 years of service life, and applied the finite element solution of the convection-diffusion problem for fitting with the experimentally obtained data. They concluded that considering only diffusion as transport mechanism did not allow a good prediction of the chloride profiles, and accounting for capillary suction due to moisture gradients permitted a better interpretation of the material's behavior. Zhang et al. [17] stated that in natural environment, the cover layer of reinforced concrete structures was affected by periodic variations of external relative humidity. Hence, they determined a method coupling a moisture transport model with hysteresis modelling. It was found that all comparisons and investigations enhanced the necessity of considering hysteresis to quantify moisture transport under repeated drying-wetting boundary conditions.

Although all the aforementioned computational methods are applicable for predicting the transport of chloride ions in unsaturated concrete, there are two issues to be addressed. First, although some study used simple closed-form solution for predicting the transport of chloride ions in unsaturated concrete, they are unable to capture the situation possessing both convection and diffusion in unsaturated concrete. This statement agrees with the limitation of the Fick's second law as reviewed by Andrade et al. [18]. On the other hand, they stated that the skin of the concrete surface behaved usually different than the concrete bulk, and the skin of the concrete might exhibit a different diffusion coefficient than the interior one modifying the profile and showing a maximum in the chloride concentration. Second, there is no closed-form solution suitable for predicting the transport of chloride ions in unsaturated concrete, because most of available computational methods are developed in a numerical approach, e.g., the Nernst-Planck based multi-species approach in the finite element method. Although this approach was the most complete, a great number of input data required made this approach inappropriate in many situations [19], e.g., probabilistic study. Due to these two issues, a new development is required to bridge the gap. Therefore, this study aims at proposing a set of new closed-form solutions for predicting the transport of chloride ions in unsaturated concrete. The proposed solutions can be used in the situation that possesses both convection and diffusion which occurs due to the wet-dry cycles of chloride transport. The proposed solutions are further developed from the bilinear closed-form solutions proposed in the previous study [20], therefore it will be first reviewed in the next section.

#### 2. Review of closed-form solutions

For assessing the transport of chloride ions in concrete in form of the diffusion, the one-dimensional partial differential equation (1-D PDE) of the Fick's second law [21] can be written as

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial C}{\partial x}$$
(1)

where *C* and *D* are defined as the chloride content as a function of position *x* and time *t*, and the chloride diffusion coefficient, respectively. To simplify the chloride diffusion prediction in concrete, a closed-form solution for Eq. (1) is necessary. To take care of this, researchers applied the mass transport model derived by Crank [21]. For example, Collepardi et al. [22] first used the closed-form solution for constant surface chloride *C*<sub>S</sub> to predict the diffusion of chloride ions in concrete as follows

$$C(x,t) = C_s \, erfc \frac{x}{2\sqrt{Dt}} \tag{2}$$

where *D* is a constant diffusion coefficient, while  $erfc(\cdot)$  is the complementary error function. It is noted that  $C_s$  and *D* are considered as the boundary condition and the material property, respectively, in numerical analysis. To predict the transport of chloride ions, both  $C_s$  and *D* can be determined by curve fitting with experimental data.

Recently, Petcherdchoo [23] included the linear surface chloride function, i.e.,  $C_S = kt$ , in modelling the transport of chloride ions in metakaolin concrete structures under chloride environment. The closed-form solution was written as

$$C(x,t) = kt \left[ \left( 1 + \frac{x^2}{2Dt} \right) erfc \left( \frac{x}{2\sqrt{Dt}} \right) - \left( \frac{x}{\sqrt{\pi Dt}} \right) exp \left( -\frac{x^2}{4Dt} \right) \right]$$
(3)

where k is a constant related to the linear function of exposure time t, and D is a constant diffusion coefficient. It is noted that the value of k and D can be determined by curve fitting with experimental data.

In many cases, a single form of surface chloride function in Eqs. (2) or (3) is not enough [24] due to some reasons as follows. First, the linear surface chloride function for Eq. (3) continuously increases when the time increases. However, this is inapplicable, because the surface chloride in the real practice will approach a constant value after a period of exposure. Second, Thomas and Bentz [25] stated that after a time period of surface chloride increase, the surface chloride started to be constant. The starting time was equal to 10 years for marine splashing zone, and 15 years or more for the atmosphere in coastal area. Hence, a mixed form of surface chloride function, i.e., a mixture of linearly increasing and

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