Ocean Engineering 191 (2019) 106549
https://doi.org/10.1016/j.oceaneng.2019.106549
Received 29 July 2019;
Received in revised form 30 September 2019; Accepted 5 October 2019.

An analytical solution for chloride diffusion in concrete with considering binding effect

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ABSTRACT

This paper presents a novel analytical solution for the chloride diffusion problem in concrete when chloride binding is taken into account. The analytical solution is obtained by splitting bound chlorides into chemically-bound and physically-bound chlorides. The former is treated as moving particles that are trapped in randomly distributed immobile holes. The latter is modelled using a linear binding isotherm. Under this assumption the original problem of diffusion with binding can be transformed to the problem of diffusion with a moving boundary for which an analytical solution can be developed. The present solution is validated using existing experimental data.

Keywords: Chloride diffusion; binding; concrete; moving boundary; analytical solution.

1. Introduction

Chloride-induced reinforcing steel corrosion is a major problem for the reinforced concrete structures that are exposed to marine environment. In order to protect the reinforcing steel from corrosion one has to understand how chlorides penetrate in concrete and how the individual components used in concrete mixture affect the chloride penetration. In early studies chloride ingress in concrete was approximated as a diffusion process [1,2,3,4,5,6], in which only parameters used to describe the chloride penetration in concrete are the surface concentration and diffusion coefficient of chlorides. However, concrete is a porous material the transport of chlorides in porous materials is significantly different from that in ideal solutions. Besides, chloride penetration in concrete involves not only the diffusion of chloride ions in pore solution of the concrete but also the physical and chemical interactions between chloride ions and pore surfaces within the cement matrix [7,8,9,10]. To accurately describe the chloride ingress in concrete, attempts were made to modify the diffusion model by including chloride binding [11,12,13,14,15,16,17,18,19], in which the total chlorides were divided into two parts; namely the free and bound chlorides. It was assumed that the transport of the free chlorides in concrete could follow the Fick's second law; whereas the bound chlorides in concrete were absorbed physically and/or chemically by the cement matrix of concrete. Experimental studies on chloride binding in different types of concrete have shown that the use of supplementary cementitious materials in concrete can have significant influence on chloride binding and thus also on the transport of chlorides in the concrete [20,21].

The incorporation of chloride binding into chloride transport model can more accurately predict the chloride ingress as well as quantify the influence of binder materials on chloride penetration in concrete. However, it also complicates the problem. For the classical diffusion problem one can find an analytical solution using error function. When the chloride binding is involved in the diffusion equation, however, the related parabolic partial differential equation involves a concentration-dependent coefficient, which makes it difficult to obtain an analytical solution. Currently, only numerical solutions are available for the diffusion problems when chloride binding is also considered [14,15,16,17,18,19]. In this paper, we have managed to develop an analytical solution for chloride transport in concrete when its binding is also considered. This is achieved by splitting the bound chlorides into chemically-bound and physically-bound chlorides. The former is treated as moving particles that are trapped in randomly distributed immobile holes. The latter is modelled using a linear binding isotherm. The analytical solution developed is validated using existing experimental results.

2. Chloride diffusion with considering chloride binding

Consider the transport of chlorides in concrete. The mass change of the total chlorides in a unit volume of concrete in a time interval dt can be expressed as follows,

$$\frac{\partial C_T}{\partial t} = -\nabla \cdot J \tag{1}$$

where C_T is the content of total chlorides in concrete, t is the time, and J is the flux of chlorides. In order to consider chloride binding, the total chlorides are divided into free and bound chlorides [22,23,24]; whereas the bound chlorides are further split into chemically-bound and physically-bound chlorides [15,25], as follows,

$$C_T = C_f + S_c + S_p \tag{2}$$

where C_f is the content of free chlorides, S_c is the content of chemically-bound chlorides, and S_p is the content of physically-bound chlorides (see Fig.1).

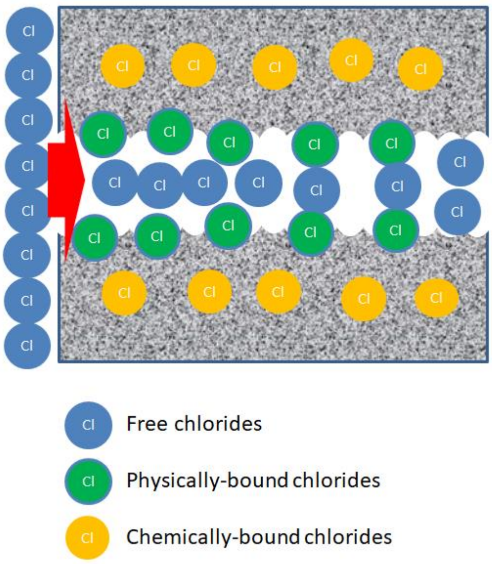

Fig.1. A schematic description of chloride transport in concrete.

The chemical binding of chlorides herein is assumed to be irreversible and the corresponding binding process can be treated as the diffusion problem of particles which are trapped in randomly distributed immobile holes. The physical binding of chlorides is assumed to be reversible and the physically-bound chlorides can be treated as immobile "free chlorides", which can be modelled using a chloride binding isotherm (see Fig.2). The flux of chlorides in Eq.(1) is contributed only by the free chlorides and can be expressed in terms of the contents of free and physically-bound chlorides as follows [25],

$$J = -\frac{D_e}{\varepsilon}\frac{C_f}{C_f+S_p}\nabla\left(C_f + S_p\right) \quad (3)$$

where D_e is the effective diffusion coefficient of chloride ions and ε is the porosity of concrete.

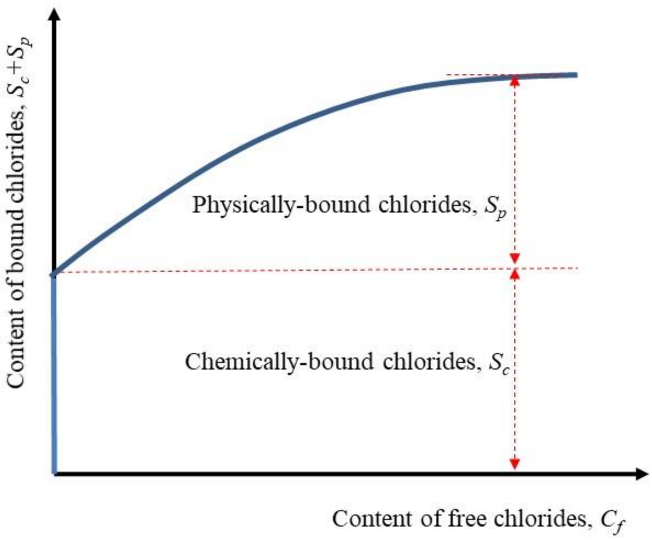

Fig.2. Illustration of chemically-bound (S_c) and physically-bound (S_p) chlorides.

When the chlorides diffuse into concrete, they will first react with the cement matrix of concrete to form chemically-bound chlorides. As soon as the chemically-bound chlorides are saturated at a place, the free chloride ions move forward. During the forward movement of free chlorides, part of them is absorbed on the pore surface to form physically-bound chlorides. Hence, the transport of chlorides in the concrete with uniformly distributed porosity can be defined separately in two different zones. One is the diffusion zone in which the chemically-bound chlorides are already saturated. There is no chemical binding taking place in that zone. The other is the trapped zone in which the chemically-bound chlorides are not saturated. Any free chlorides diffusing into that zone will be trapped by chemical binding. The boundary between the two zones is defined by the diffusion front of free chlorides or the saturation front of chemically-bound chlorides. Fig.3 schematically describes the variations of the free, physically-bound, and chemically-bound chlorides in the two zones. Substituting Eqs.(2) and (3) into (1) and noting S_c is constant in the diffusion zone, it yields,

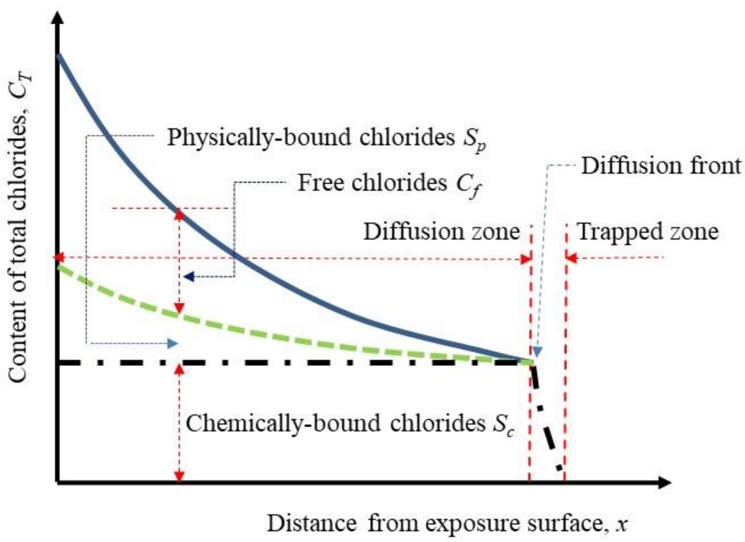

Fig.3. Schematic distribution profiles of chlorides in concrete.

$$\frac{\partial (C_f+S_p)}{\partial t} = \nabla\left[\frac{D_e}{\varepsilon}\frac{C_f}{C_f+S_p}\nabla\left(C_f+S_p\right)\right] \qquad 0 < x < \xi(\mathrm{t}) \qquad (4)$$

The initial and boundary conditions of free chlorides $C_f(t,x)$ can be expressed as follows,

$$C_f(0, x) = 0 \tag{5}$$

$$C_f(t, 0) = C_s \text{ and } C_f(t, \xi) = 0 \tag{6}$$

where ξ is the time-dependent coordinate representing the depth of the diffusion front, which moves forward when time increases and C_s is the content of free chlorides on the concrete exposure surface. For a given binding isotherm the content of physically-bound chlorides can be expressed in terms of the content of free chlorides. Thus, Eqs.(4)-(6) represent the diffusion problem with a moving boundary. It is obvious that the solution of Eqs.(4)-(6) also depends on the binding isotherm function of $S_p = f(C_f)$. For a linear binding isotherm of $S_p = \alpha C_f$ where α is a constant Eq.(4) becomes a linear parabolic partial differential equation and can be simplified as follows,

$$\frac{\partial C_f}{\partial t} = \nabla\left(\frac{D_e}{\varepsilon(1+\alpha)}\nabla C_f\right) \qquad 0 < x < \xi(t) \tag{7}$$

For the diffusion problem governed by Eq.(7), the depth of the diffusion front is proportional to square root of the diffusing time [26]. Thus, the following expression can be assumed for ξ(t),

$$\xi(t) = k_\xi \sqrt{Dt} \tag{8}$$

where D=D_e/[ε(1+α)] and k_ξ is a constant to be determined. The solution of Eq.(7) with the initial and boundary conditions defined by Eqs.(5) and (6) can be expressed as follows [26],

$$C_f(t,x) = C_s\left(1 - \frac{erf\left(\frac{x}{2\sqrt{Dt}}\right)}{erf\left(\frac{k_\xi}{2}\right)}\right) \qquad 0 \le x \le \xi(\mathrm{t}) \tag{9}$$

where $erf(\cdot)$ is the error function. It is obvious from Eq.(9) that if k_ξ is known then the solution (9) for $C_f(t,x)$ is completely defined. In order to determine k_ξ an additional mass conservation equation needs to be developed at the point of the diffusion front, which can be expressed as follows,

$$-\frac{D_e}{\varepsilon}\frac{\partial C_f}{\partial x} = S_c\frac{d\xi}{dt} \qquad \text{at } x = \xi(\mathrm{t}) \tag{10}$$

Physically, the left-hand-side of Eq.(10) represents the diffusion flux from the diffusion zone into the trapped zone; whereas the right-hand-side of Eq.(10) represents the flux required in order that the diffusion front can advance by a distance of $d\xi$ in the time interval of dt. Substituting Eqs.(8) and (9) into (10), it yields,

$$\frac{k_\xi}{2} erf\left(\frac{k_\xi}{2}\right) exp\left(\frac{k_\xi^2}{4}\right) = \frac{(1+\alpha)C_s}{\sqrt{\pi}S_c} \tag{11}$$

Eq.(11) is a nonlinear algebraic equation about k_ξ, which can be used to determine k_ξ for a given ratio of $(1+\alpha)C_s/S_c$. After k_ξ is determined it can be substituted into Eq.(8) for calculating the depth of diffusion front $\xi(t)$ and Eq.(9) for calculating the concentration profile $C_f(t,x)$ of free chlorides directly. The content of the total chlorides can be calculated using Eq.(2).

Note that, in the trapped zone there are no free chlorides and the content of chemically-bound chlorides could be any value between 0 and S_c, indicating that the solution in the trapped zone is of singularity. Also, since the chemically-bound chlorides are not able to transport the trapped zone is in fact infinitely small. In other words, both the fronts of the diffusion zone and trapped zone move forward at the same time.

3. Experimental validation of analytical solution

The analytical solution described above is now used to simulate the chloride diffusion experiments (ponding tests) reported by Qiao et al. [27]. In the diffusion experiments, ordinary Portland cement (OPC) concrete specimens with water-to-cement ratios of 0.3, 0.4, 0.5 and 0.6 were mixed, in which the proportions of sand and gravel were kept unchanged with the values of 616 kg/m^3 and 1050 kg/m^3, respectively. The proportion of OPC used was 480, 420, 370 and 325 kg/m^3 for 0.3, 0.4, 0.5 and 0.6 water-to-cement ratio concrete. The density of the concrete calculated based on the mixing proportion is 2449, 2413, 2380 and 2345 kg/m^3 for 0.3, 0.4, 0.5 and 0.6 water-to-cement ratio concrete. The porosities of the concretes with water-to-cement ratio of 0.3, 0.4, 0.5 and 0.6 are assumed to be 0.10, 0.12, 0.135 and 0.15, respectively. The specimens were immersed in the solution of chloride concentration 5 mole/l for four months. After then powder samples were taken at different depths from the tested specimens, from which the total chloride contents were determined.

In the analytical solution, the surface concentration of free chlorides, C_s, in the unit of wt.% of concrete is calculated as follows,

$$C_s = \frac{5\times35.5\times100\times\varepsilon}{\rho_{con}} \tag{12}$$

where ρ_{con} in kg/m^3 is the density of the concrete and the number of 35.5 in the right hand side of Eq.(12) is the molar mass of chloride molecule. The concentration of chemically-bound chlorides, S_c, in the unit of wt.% of concrete and the dimensionless parameter α describing the physically-bound chlorides are assumed as follows, which is based on the binding isotherm provided in [27],

$$S_c = 0.4\rho_{cem} \tag{13}$$

$$\alpha = 0.255 \tag{14}$$

where ρ_{cem} is the relative weight of cement product (cement plus water) in concrete. The effective diffusion coefficient of chloride ions is assumed as follows,

$$D_e = 8.27 \times 10^{-11} w^{2.55} \varepsilon \tag{15}$$

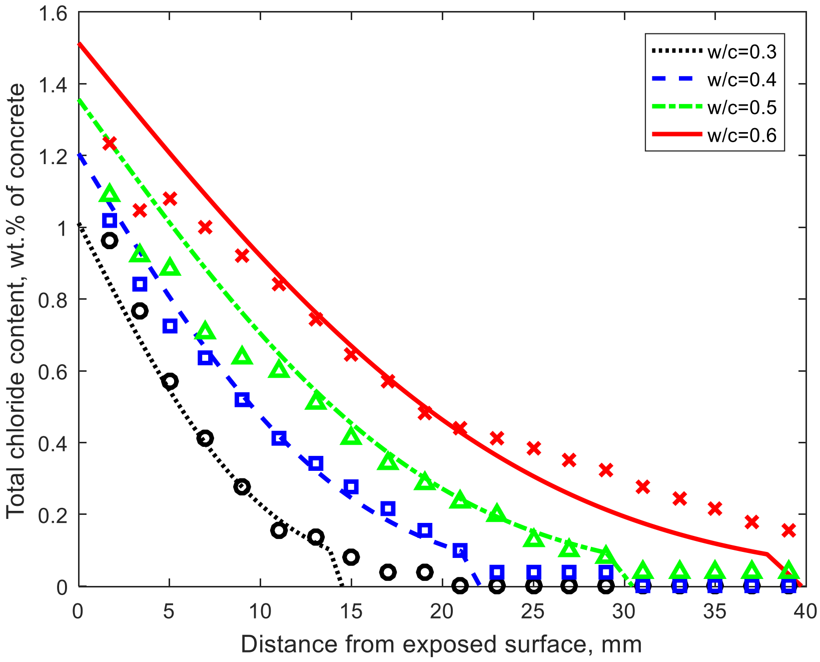

Fig.4. Experimental validation of present analytical solutions (data points are experimental results from [27]).

where *w* is the water-to-cement ratio. The comparison between the simulated total chlorides and experimentally obtained total chlorides is shown in Fig.4. It can be seen from the figure that the predicted total chloride distribution profiles for concrete specimens with different water-to-cement ratios are all in reasonably good agreement with the experimental data. Note that the experimental data are the average of the two samples. In the original data [27], there were big variations for the samples with high water-to-cement ratios (0.5 and 0.6) and close to the exposed surface (less than 10 mm). Thus, although the predicted curves shown in Fig.4 for samples with water-to-cement ratio 0.5 and 0.6 are slightly higher than the experimental data, they are still in the variation ranges of the experimental results. This indicates that the present model is able to represent the main transport features of chlorides in concrete.

4. Conclusions

In this paper, we have presented a novel analytical solution for chloride diffusion in concrete, which takes account the effect of chloride binding. By splitting the bound chlorides into chemically-bound and physically-bound chlorides, the original problem of diffusion with chloride binding is transformed to the problem of diffusion with a moving boundary for which an analytical solution can be developed. The present solution has been validated by using the experimental data published in literature. The comparison of the distribution profiles of total chlorides predicted by using the present analytical solution and those measured in experiments has demonstrated the capability and rationality of the present analytical model.

Acknowledgements

The authors would like to acknowledge the financial support received from the National Natural Science Foundation of China (Grant No. 51520105012). Part of the present work was also supported by the European Commission Research Executive Agency via a Marie Skłodowska-Curie Research and Innovation Staff Exchange project (H2020-MSCA-RISE-2017, TRAC-777823).

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