

Chloride Diffusion in Concrete Exposed to Wetting and Drying Cycles

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Abstract – This paper presents a double-porosity model for simulating chloride diffusion in concrete exposed to wetting and drying conditions. The two porosities used in the model corresponding to nano and micro pores with different transport properties existing in concrete. Chloride ingress and moisture transport in concrete is explained by Fick's law and Darcy's law, respectively. The model is used to explore the moisture effect on chloride diffusion in concrete. The numerical results show chloride and moisture profiles in concrete and they revealed that moisture variation has strong influence on chloride transport. The wetting and drying cycles can accelerate the diffusion mechanism of chloride from exposed surface into inside of concrete sample.

Keywords: Concrete, Chloride, Moisture, Wetting and Drying, Durability

1. Introduction

Concrete is considered as a porous material with pore sizes ranging from a few tenths of nanometres to several tens of micrometres. If the pores are filled with water, concrete is to be fully saturated while if they are occupied by water and air, it is referred to as non-saturated concrete. The moisture effect plays a very important role when concrete is in non-saturated condition and/or subjected to wetting and drying cycles. For example, if the moisture content inside concrete is less than its saturation level, water will be absorbed into concrete by large capillary forces initiating from the contact of the very small pores of concrete with the liquid phase [1]. Corrosion of reinforcing steel due to chloride attack is one of the severe problems for long term durability of reinforced concrete structures. Most of reinforced concrete structures are under non-saturated condition in which chloride ingress into concrete by two driving forces, chloride and moisture gradients, that chloride ions are carried by moisture movement [2]. The previous study of Thomas and Matthews [3] have shown that chloride penetration into concrete subjected to wetting and drying cycles is remarkably different from that is saturated condition. It was also found that chloride diffusion mechanism in concrete exposed to wetting and drying action is quite different from those in fully saturated condition [4]. Several models have been developed to describe the water and chloride transport in concrete. For instance, [5] proposed a model of multi-species diffusion in concrete by considering electrostatic potential and ionic coupling interaction between different ionic species. A chloride transport model taken into account the effect of both initial and surface saturation due to wetting and drying cycles has been proposed by Jin et al. [4]. Bastidas- Arteaga *et al.* [6] studied chloride penetration in unsaturated concrete using a probabilistic mathematical model taken into account random variables to represent the model parameters, material properties, and stochastic processes to environmental actions. Sleiman *et al.* [7] presented a numerical model and conducted the experimental study to validate the numerical results obtained from the model on chloride transport in partially saturated concrete coupled with moisture transport in the concrete. The electrical double layer has been included in the physical model for chloride penetration into non-concrete proposed by Nguyen and Amiri [8] which was solved by multi-component ionic transport equations coupled with those of humidity. Wang and Ueda [9] presented a lattice

network model based on the mesoscale composite structure of concrete to analyze the penetration property of concrete; especially the effects of microcracking induced by freeze-thaw damage on the unsaturated flow behavior. Recently, Geng *et al.* [10] developed a novel coupled transport model of ionic species and ionic solution in unsaturated concrete by accounting for the osmotic effect of ionic concentration on the transport of ionic solution due to the small pore sizes in concrete.

Thus, to better understand the transport mechanism of moisture and chloride in non-saturated concrete, it is necessary to distinguish the transport features of the micro- and nano-scale pores in concrete. In the present study, a double-porosity model describing the chloride and moisture transport in non-saturated concrete is presented. Moisture and chloride diffuse in concrete through two porosities, large and small pores groups, is derived based on Darcy's and Fick's law, respectively, with different defined transport properties. The mass exchange of two pores was taken into account to describe the interflow between them.

2. Double-Porosity Diffusion Model

The concept of the double-porosity has been studied by many researchers and applied for several diverse problems such as a single phase within a naturally fracture reservoir, water flow in dolostones, ionic transport in soils, ionic solution flow in fracture rocks, groundwater flow, waste and contaminant transport in soils, fluid flow in pavement, chloride penetration into concrete, the acoustic modelling of perforated concrete, and moisture flow induced creep in concrete [11-16]. In the present study, the governing equations of moisture and chloride transport in concrete will be formulated based on Darcy's law and Fick's law, respectively, associated with double-porosity model.

2.1. Moisture and Chloride Diffusion in Concrete

The governing equations of moisture transport in concrete based on Darcy's law incorporated with double-porosity model will be introduced briefly in this study. More details can be found in Li *et al.* [1]. Moisture transport in each pore group can be described as,

$$\frac{\partial(\phi_1 \rho_1)}{\partial t} = -\nabla(\phi_1 \rho_1 V_1) + R_{12} \quad (1)$$

$$\frac{\partial(\phi_2 \rho_2)}{\partial t} = -\nabla(\phi_2 \rho_2 V_2) - R_{12} \quad (2)$$

in which ρ_1 and ρ_2 are the densities of moisture in small and large pores, respectively. V_1 and V_2 represent the flow velocities of moisture in small and large pores, respectively, and R_{12} in $\text{kg}/(\text{m}^3\text{-s})$ is the mass exchange rate of the moisture between the small and large pores. Based on Darcy's law, the flow velocity of the moisture in porous media can be given in terms of water pressure. So, V_1 and V_2 can be written as follows,

$$V_i = -K_i \nabla P_{il} \quad (i = 1, 2) \quad (3)$$

where K_i in $\text{m}^4/(\text{N}\cdot\text{s})$ is a constant described by the hydraulic conductivity and P_{il} is the water pressure, which can be given by

$$P_{il} = P_{ig} - P_{ic} \quad (i = 1, 2) \quad (4)$$

in which P_{ig} is the partial pressure in the gas phase and P_{ic} is the capillary pressure. It is assumed that the air in the gas phase is the ideal gas expressed as

$$P_{ig} = P_{atm} \quad (i = 1, 2) \quad (5)$$

where $P_{atm} = 101,325 \text{ Pa}$ is the standard atmosphere pressure and the capillary pressure is approximated as

$$P_{ic} = \alpha_i P_{atm} \left(e^{\beta_i(1-\theta_i)} - 1 \right) \quad (i = 1, 2) \quad (6)$$

in which α_i and β_i are the dimensionless constants obtained by using experimental data, $\theta_i = \rho_i / \rho_w$ is the degree of saturation and $\rho_w = 1,000 \text{ kg/m}^3$ is the density of water. Substituting Eqs. (3)-(6) into (1) and (2), it gives,

$$\frac{\partial(\theta_1)}{\partial t} = \nabla(D_{\theta_1} \nabla \theta_1) + \frac{R_{12}}{\rho_w \phi_1} \quad (7)$$

$$\frac{\partial(\theta_2)}{\partial t} = \nabla(D_{\theta_2} \nabla \theta_2) - \frac{R_{12}}{\rho_w \phi_2} \quad (8)$$

where D_{θ_i} (m^2/s) is the moisture diffusivity which can be given by,

$$D_{\theta_i} = K_i \theta_i \frac{dP_{il}}{d\theta_i} = -K_i \theta_i \frac{dP_{ic}}{d\theta_i} = K_i \alpha_i \beta_i P_{atm} \theta_i e^{\beta_i(1-\theta_i)} \quad (i = 1, 2) \quad (9)$$

As seen from Eq. (9), the moisture diffusivity is dependent on a function of degree of saturation. In order to solve θ_1 and θ_2 from in Eqs. (7) and (8), the mass exchange between the small and large pores is need to be determined that is,

$$R_{12} = k_{12} \rho_w (P_2 - P_1) \quad (10)$$

where k_{12} ($\text{m}^2/\text{N-s}$) is the constant [1] and P_i is the average pore pressure. It is noted that if the pore is not saturated, the total pore volume is occupied by both air and water. Therefore, the average pore pressure can be described as,

$$P_i = (1 - \theta_i) P_{ig} + \theta_i P_{il} \quad (i = 1, 2) \quad (11)$$

Substituting Eqs. (4) – (6) into (11), it gives,

$$P_i = P_{atm} \left[1 - \alpha_i \theta_i \left(e^{\beta_i(1-\theta_i)} - 1 \right) \right] \quad (i = 1, 2) \quad (12)$$

Assume that the pores are connected not only within each of pore groups but also between the groups. This implies that chloride ions can transport not only with the group but also between the groups. If the pores are not fully saturated, the governing equations describing the chloride transport in concrete pore solution can be derived in terms of moisture dependent in a representative elementary volume of the concrete as follows,

$$\frac{\partial(\theta_1 C_1)}{\partial t} = \nabla(D_{C_1} \nabla \theta_1 C_1) + k_{ex} (\theta_2 C_2 - \theta_1 C_1) \quad (13)$$

$$\frac{\partial(\theta_2 C_2)}{\partial t} = \nabla(D_{C_2} \nabla \theta_2 C_2) - k_{ex} (\theta_2 C_2 - \theta_1 C_1) \quad (14)$$

where C_1 and C_2 are the chloride concentration in small and large pores, respectively. D_1 and D_2 represent chloride diffusion coefficient in small and large pores, respectively. During the transport process, it is assumed that there will be some mass exchange between two pore groups. The exchange rate is related to their chloride concentrations that k_{ex} is the exchange rate constant of chloride between two pore groups determined by the best fit of experimental data and numerical simulation [17].

3. Numerical Examples

Numerical examples in this study are divided into three cases surrounded with the variation of degree of saturation. All concrete specimens herein are exposed to 0.513 mol/l of NaCl solution from its one side with all other sides sealed and initial chloride concentration inside specimens is 0 mol/l. The chloride penetration depth is measured from the top to bottom surface of the concrete specimen. The first case is for fully saturated concrete sample that the degree of saturation at the exposed surface and inside is $\theta_{exp} = 0$ and $\theta_{ins} = 1.0$, respectively, as

shown in Figure 1. In the second case, concrete is in non-saturated condition in which the equivalent degree of saturation at the exposed surface and inside is $\theta_{exp} = 1.0$ and $\theta_{ins} = 0.25$, respectively, as illustrated in Figure 2. Figure 3 exhibits the third case which is for the concrete specimen subjected to the wetting and drying cycles at the exposed surface, the change between wetting ($\theta_{exp} = 1.0$) and drying ($\theta_{exp} = 0.25$) with a period of time following sine function pattern as plotted in Figure 4.

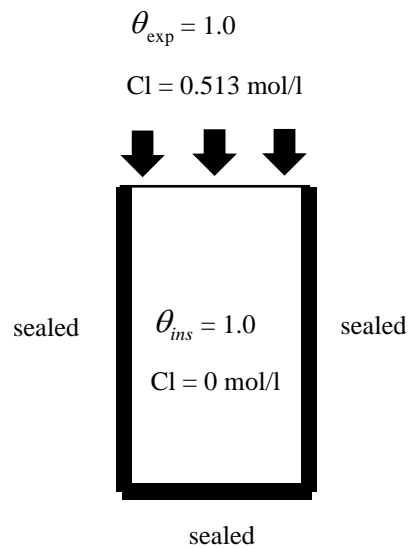


Figure 1. A fully saturated concrete sample exposed to chloride solution at the top surface.

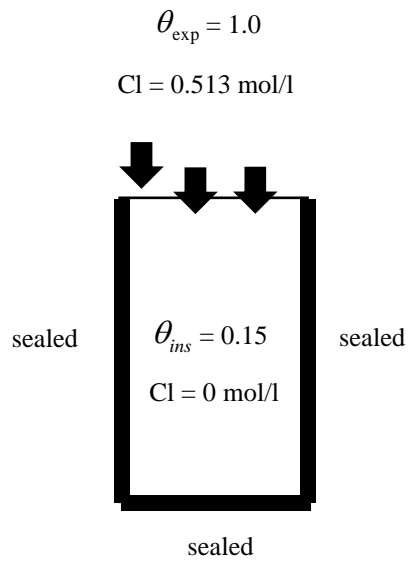


Figure 2. A non-saturated concrete sample exposed to chloride solution at the top surface.

the wetting and drying cycles ($\theta_{exp} = 1.0$ and $\theta_{exp} = 0.25$)

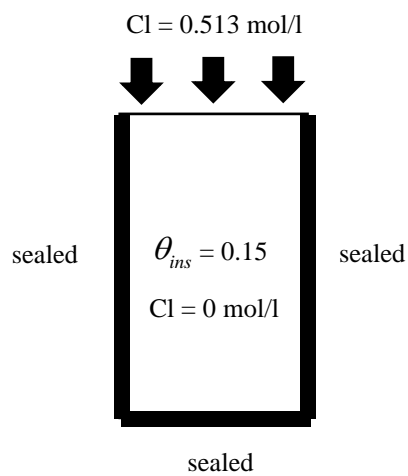


Figure 3. A non-saturated concrete sample exposed to chloride solution and the wetting and drying cycles at the top surface.

4. Numerical Results and Discussion

The profiles of free chloride concentration of concrete in fully saturated condition at different times of exposure is in Figure 5. The depth of chloride penetration is measured from the top surface of concrete sample. It can be seen from Figure 5 that the free chloride concentration decreases with increasing depth from the top surface (the initial chloride concentration inside the concrete is zero). At a fixed depth, when the exposure time is longer the free chloride is higher.

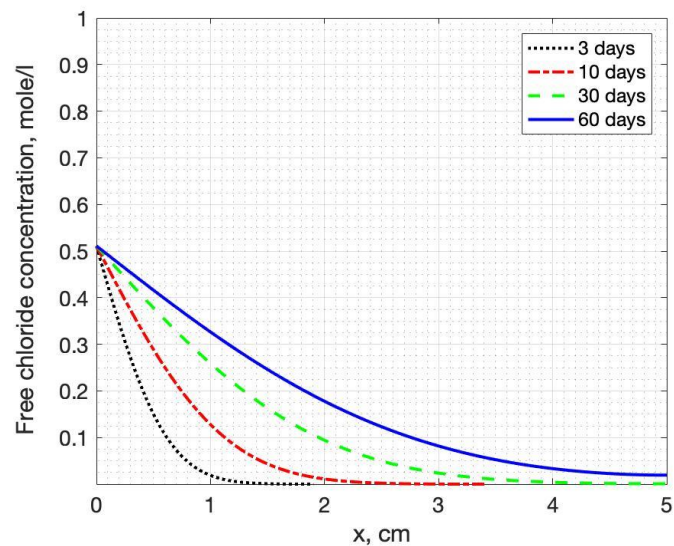


Figure 5. Chloride profiles of concrete in fully saturated condition at different times of exposure (case 1).

Figure 6 shows the chloride profiles at 3, 10, 30 and 60 days of exposure in non-saturated condition. The degree of saturation outside (at the exposed surface) and inside specimen is $\theta_{exp} = 1.0$ and $\theta_{ins} = 0.15$, respectively. It can be seen from Figure 5 that chloride concentration is higher than that of fully saturated concrete (Figure 4). This is because moisture gradient moves from the exposed surface to inside of concrete specimen. In fact, the moisture gradient is in the same direction of the gradients of chloride and thus the moisture movement can carry these ions accelerating the penetration rate of chloride ions. It can be concluded that the moisture condition has significant influence on the diffusion of chloride ions in concrete by accelerating the penetration rate of chloride.

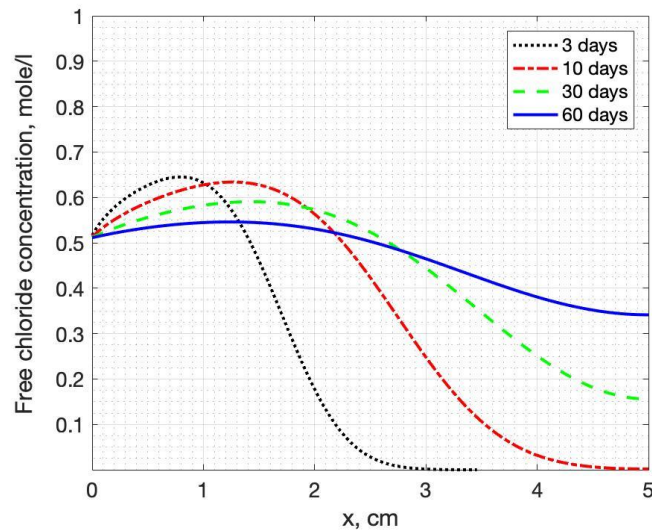


Figure 6. Chloride profiles of concrete in non-saturated condition at different times of exposure (case 2).

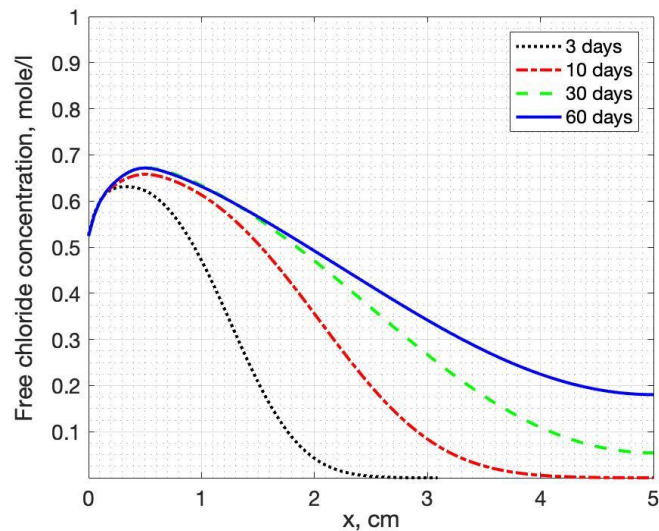


Figure 7. Chloride profiles of concrete exposed to wetting and drying cycles at different times of exposure (case 3).

Figure 7 illustrates the chloride profiles due to the variation of the degree of saturation in the concrete after the drying and wetting (described in case 3) action in 3, 10, 30, and 60 days. It can be seen from the figure that concrete subjected to wetting and drying cycles, the transport of chloride ions represents a combination of diffusion and convection. The numerical results show that the depth of the convection zone mainly varies from near the exposed surface. As noticed that the action of convection mainly occurs in the skin convection zone, the diffusion can be regarded as the dominant process for chloride transport in the deeper concrete.

4. Conclusion

In this work, a double-porosity model for simulating chloride transport in concrete exposed to wetting and drying condition is presented. The model was used to determine chloride concentration profiles in concrete in response to externally applied wetting and drying cycles. From the present study, the following conclusions can be drawn:

- Compared to the various existing chloride diffusion models, using two porosities classified by pore size taken into account mass exchange between two porosities, the present model can appropriately reflect to both chloride and moisture transport in concrete.
- Moisture variation has a remarkable influence on the chloride distribution profiles, particularly on the near surface exposed to wetting and drying cycles.
- During wetting and drying cycles, the desaturation zone in concrete created in the first cycle expands continuously the subsequent wetting-drying cycles. This can push chloride ions from the surface layer into inside concrete leading to accelerate the initial corrosion time.
- Compared to the traditional Fick's law model considered average pore sizes, the present model is more detailed and able to give out the pore size effect on chloride diffusion in concrete.
- The prediction model proposed in this study can be further developed to investigate how the arrangement of sensors implemented in the chloride sensing systems affects the variability in the predicted time to corrosion initiation. This will be beneficial for the structure owners and management agencies in providing useful information such that proper decision can be made for early warning system, repair, and rehabilitation.

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