



Study of electrical double layer effect on chloride transport in unsaturated concrete



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HIGHLIGHTS

- The EDL effect is more significant in the saturated concrete than the unsaturated one.
- The chloride concentration is increased only when the sign of zeta potential is negative.
- In the considered concretes, slag develops an EDL effect more than fly ash.

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ABSTRACT

In this paper, a physical model of chloride ingress concretes is proposed. The originality of the model lies in its consideration of electrical double layer (EDL) phenomenon in unsaturated concrete. The EDL is occurring at the interface between pore walls and pore solution. The work is performed by solving the multispecies ionic transport equations coupled with those of humidity. To show the effect of slag and fly ash, several concretes were considered. The chloride profile was simulated. The results show that chloride concentration increase for EDL negative more than EDL positive. The EDL effect is reduced in unsaturated concrete due to discontinuity of liquid phase. Finally, it is also shown that the concrete containing slag develops and EDL more important than those manufactured with fly ash.

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1. Introduction

The corrosion of steel reinforcement is one of the most important causes of degradation of concrete structures. The corrosion is due to chloride ingress mainly in the coast zones. In fact, when the chloride concentration reaches the threshold value, the corrosion of steel began until the local ruin of the structure according to TUTTI model [1,2]. Consequently, the service life of the structures is reduced.

To predict correctly the service life, it is important to take into account in the chloride transfer model, the main chemical and physical phenomena's occurring in cement based materials such the chemical binding, the activity of pore solution, the electrostatic interaction between the ions contained in the pore solution and the electrical double layer (EDL).

Several models have been developed during the two last decades. Some models are monospecies, based on modified Fick's law [3–5] have just taken into account the chemical binding of chloride through the isotherm (Freundlich or Langmuir). Other models [6,7] considered as “multispecies” are based on Nernst-Planck equation. These models are more consistent, because in addition to chloride chemical binding they take into account some physical phenomena mainly the interaction between chloride and other ions contained in the pore solution of concrete and electrocapillary process occurring between the pores walls and the pore solution. This process known under “electrical double layer (EDL)” induces a viscous electric effect which slowed the chloride ingress [7]. Also, in other fields such nanofiltration membranes and clays, the EDL takes a significant role in the transport of ions.

In the field of cement based materials, Chatterji and Kawamura [8] were the first who studied the EDL effect on ionic transport, but qualitatively. We can also note the several studies of Nägele [9–15] which deal only with the measurement of zeta potential considered as the main parameter of EDL. But to our knowledge, the studies dealing with the EDL effect on chloride transport from qualitative point of view, mainly in unsaturated concrete, are few. So the

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goal of this work is to highlight the EDL effect in unsaturated concrete submitted to chloride ingress. To reach this aim, we have to combine ions and humidity transport with the EDL effect at macroscopic scale stems from Poisson–Boltzmann equation. Simulation of chlorides profiles in concretes containing fly ash and slag were carried out to show the effect of the sign of EDL on chloride ingress.

2. Electrical double layer (EDL) phenomenon: brief description

In order to understand the EDL effect, we just give a brief description of this phenomenon. More details are given in [7].

The Stern model (Fig. 1) is generally adopted to describe EDL phenomenon. At the interface between the pore walls (cement matrix) and the pore solution, ions are physically adsorbed by Van der Waals ‘forces. An imbalance ionic is then established, but the bulk remains in equilibrium.

The interface is structured in two parts, a compact (Helmholtz) layer ($x \leq x_2$) and a diffuse layer (from x_2 to the bulk): the two parts constitutes the electrical double layer. The compact layer ($x \leq x_2$) is made of solvated ions, adsorbed at the surface. The potential in the EDL due to the imbalance ionic follows to the Poisson equation. At the compact layer, the potential is known as “zeta potential” and can be measured by a zeta meter. The extension of the potential is occurred on a distance called “Debye length” which depends on the temperature, the ionic concentration of the bulk solution and its dielectric permittivity. In this paper, we consider that a pore of a porous medium can be schematically represented by two parallel flat plates distant from d which is considered as the pore diameter. In this case, two diffuse layers are in face to face which can overlap when the pore diameter is close to Debye length.

3. Physical modeling

3.1. Ionic transfer

In saturated medium the water movement by advection is dramatically low according to the permeability of concrete. In the unsaturated one, convection phenomena play an important role in the transfer of ions, especially in the humidification phase. By analyzing the electrochemical potential at the microscopic level, some authors [17–20] have shown that the consideration of the EDL effect leads to a change on flux of ions in cement based materials. Indeed, in the small pores size (including gel pores), electrostatic interactions occur through the EDL phenomenon between

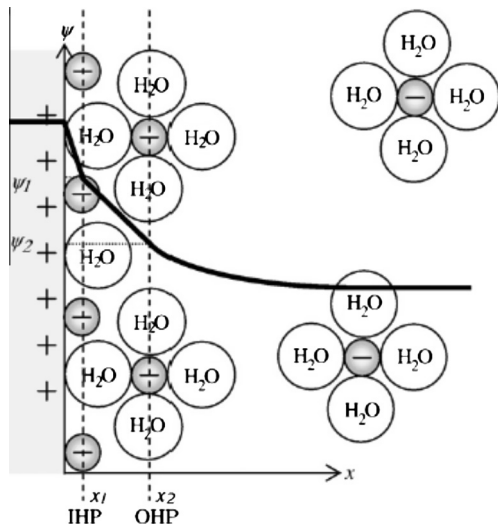


Fig. 1. Schematic view of the EDL [16].

the surface of the cement matrix and the ions contained in the pore solution. Therefore, the ion concentration is not homogeneous locally. Under these conditions, the ion flux usually based on the Nernst–Planck equation is modified [21,22]. The modification concerns the concentration of anions and cations:

$$\bar{C}_i = K_{\pm} C_i \quad (1)$$

where K_+ and K_- are two coefficients which traduce EDL effect on cation and anion fluxes, respectively. C_i is the average concentration of specie i .

By taking into account equation, the classical equation of Nernst–Planck extended to unsaturated transport, becomes:

$$\frac{\partial(wK_{\pm}C_i)}{\partial t} + (1 - \epsilon_0) \frac{\partial(K_{\pm}C_{ib})}{\partial t} - \text{div} \left(\underbrace{wD_iK_{\pm}\text{grad}C_i}_{\text{diffusion}} + \underbrace{\frac{K_{\pm}D_iFz_i}{RT}C_iw\text{grad}\Psi}_{\text{migration}} - \underbrace{K_{\pm}wC_iU}_{\text{convection}} \right) = 0 \quad (2)$$

with ϵ_0 is the porosity of the material, w is water content. C_i is the concentration of chemical specie i contained in the pore solution. C_{ib} is the concentration of specie i bound to cement matrix of the concrete. ψ is the electrical potential in the pore solution. D_i is the diffusion coefficient of the specie i and z_i is its valence. F is the Faraday’s constant, R is the gas constant and T is the thermodynamic temperature (293 °K).

In the pore solution, the ions interact with each other, producing an electrostatic potential ψ which can be deduced from Eq. (2) in the case of a natural diffusion (no current density):

$$\text{grad}\Psi = - \frac{\sum_{i=1}^n D_i K_{\pm} C_i z_i w \text{grad} C_i - \sum_{i=1}^n z_i w U K_{\pm} C_i}{\frac{F}{RT} \sum_{i=1}^n D_i K_{\pm} C_{ib} z_i^2 w \nabla C_{ib}} \quad (3)$$

$$K_+ = \frac{A(\kappa d)^2}{1 - AB\kappa d + A(\kappa d)^2} + \frac{1 + Z}{2} \frac{2q}{FdC_{pc}} \quad (4)$$

$$K_- = K_+ - \frac{2q}{FdC_{pc}} \quad (5)$$

A and B are two parameters which depend on the zeta potential and the pore diameter d , the concentration of the bulk C_{pc} , the surface density charge q and on Debye constant κ [7], Z is the sign of the EDL ($Z = 1$, EDL positive; $Z = -1$, EDL negative).

The rate of chemical chloride binding considered follows the Langmuir isotherm.

$$C_{ib} = \frac{aK_{\pm}C_i}{1 + bK_{\pm}C_i} \quad (6)$$

The constants a and b are defined in the Section 4.

3.2. Humidity transfer

The mains assumptions considered are:

- The liquid phase is constituted by water. The gas one contains dry air and steam. The pressures in these two phases are noted p_a and p_v , respectively.
- The gravity effect is negligible.

The balance equations are for each phase liquid (w) (water vapor) and air (a) are:

$$\frac{\partial[\rho_w w]}{\partial t} = -\text{div}(\rho_w v_w) - \dot{m} \quad (7)$$

$$\frac{\partial[\rho_v(\epsilon_0 - w)]}{\partial t} = -\text{div}(D_{va}\text{grad}(\rho_v)) + \dot{m} \quad (8)$$

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