Study of the chloride transport in unsaturated concrete: Highlighting of electrical double layer, temperature and hysteresis effects

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HIGHLIGHTS

- Chloride ingress in concrete depends on electrical double layer (EDL) and its sign (positive or negative).
- In the concrete containing slag, the overlapping of EDL is strong due to the thin pore size.
- The hysteresis of sorption desorption isotherm and temperature effect accelerates the chlorides transfer in the zone near the sample surface and decreases inside the sample.

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ABSTRACT

In this paper, we suggest a modelling of chloride ingress in unsaturated concretes. The originality of our model lies in its consideration of the electrical double layer (EDL), the temperature as well as the isotherm sorption-desorption hysteresis. In order to consider slag and fly ash effects, several concretes were considered and experimentally tested in tidal conditions. The chloride profile was simulated by a multi-species model. The simulations show that the chloride concentration increases with a negative EDL more than with a positive EDL and that this effect occurs mainly in the concrete containing slag where the overlapping is more important due to the pore size distribution. We also show that both temperature and hysteresis affect the chloride ingress at the surface more than in deeper layers of the concrete specimen most likely due to a drying effect. Finally, the results put forward a good agreement between measured and simulated chloride profiles mainly when the hysteresis is taken into account.

1. Introduction

The corrosion of steel in reinforced concrete is a major problem for contractors and asset owners, particularly, when constructions are located in maritime environments. In fact, the reinforced concrete structures are submitted to a chemical attack coming from the chloride ions of sea water. Chloride ions cause a decrease of pH in the pore solution around the steel and initiate the corrosion of the reinforcement bars when their concentration reaches a threshold value. In fact, the chloride attack is the first cause of bridges' deterioration in the United Kingdom [1]. In order to predict the service life of concrete structures, it is important to study the chloride ingress through concrete cover both from experimental and modelling perspectives.

In a previous work [2], we first mentioned the disadvantages of the classical modelling of chloride transfer within concrete based on Fick's law and the necessity to develop models which take into account the main physical and chemical processes occurring in the cement based materials. We offered a new model based on Nernst-Planck's equation by integrating the electrical double layer (EDL) effect in saturated concrete [3]. The simulations of chloride transfer show that the EDL sign on chloride ingress has a strong influence. The EDL considered herein is based on the Stern Model composed of Helmholtz and diffuse layers. The electrical potential at the interface between the two layers is called the "Zeta potential".

Previously, we had also discussed the effect of the electrical double layer in the ionic transfer, mainly in an unsaturated med-

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ium [2]. The EDL is chiefly quantified by the Zeta potential whose values were chosen arbitrarily. However, to predict more accurately the chloride ingress, it is important to use the real value of the Zeta potential for which we suggest and experimental investigation as an initial step for the former model improvement. In order to further increase the accuracy of the current model, we have taken into consideration the hysteresis effect during the wetting and drying cycles. In fact, water absorption capacity varies when concretes are submitted to continuous wetting and drying. Moreover, hysteresis effect appears in the majority of the studied concretes because of its ability to modify the moisture transfer within material and the ionic transfer. Therefore, an experimental study dealing with sorption-desorption isotherm has been carried out.

Previously [2], we considered isothermal conditions (temperature constant), so a third major improvement of the model consists on taking into account a combined heat and mass transfer. We must to specify that for heat transport, an empirical relationship [4] of thermal conductivity was considered.

Finally, the chloride profile simulated by a full modelling taking into account the measured Zeta potential, sorption-desorption isotherm (with hysteresis) and temperature are compared with those obtained in laboratory by using a tidal simulator.

2. Modelling of the combined transport

2.1. Moisture transfer in unsaturated porous materials

In our previous work [2], we studied the coupled transfer ions and moisture in isothermal conditions. To take into account the temperature variation ns, the present work is an attempt to express moisture transfer with the temperature variation. Consequently, the term of the temperature is developed in the equations.

A porous media such as concrete has a great complexity from a physical point of view because of the presence of three phases: solid, liquid and gas that each has specific characteristics. In order to simplify the mathematical description of the mass transfer, we admitted assumptions which are generally adopted in the literature [4,5]. These main assumptions are reminded as follows:

– the shrinkage and cracking are negligible,
– there is no deformation of the solid skeleton during the ionic transfer which means that the solid phase is indeformable,
– the concrete has a fine porosity, consequently the flow of the liquid phase is slow and laminar,
– the gas pressure is constant. We have to note that the approach considering constant gas pressure is satisfactory to describe the moisture transfer in a large number of type of concretes because the drying process is slow,
– the gravitational forces are neglected.
– the liquid phase is continuous, because if the ionic transfer could not occur either by diffusion or by convection.

To obtain a macroscopic description from a microscopic scale, we used the homogenization average method based on a definition of a representative elementary volume (REV). This method is described in the papers [6,7]. For each liquid and vapor phase, the flux is written as:

Water flux:

$$J_w = \rho_w \frac{K_w K_{rw}}{\mu_w} \left(\frac{\partial P_c}{\partial W}\right)_T gradW + \rho_w \frac{K_w K_{rw}}{\mu_w} \left(\frac{\partial P_c}{\partial T}\right)_W gradT \quad (1)$$

Vapor water flux:

$$J_v = -f_{res} D_{va} \frac{\partial \rho_v}{\partial W} grad(W) - f_{res} D_{va} \frac{\partial \rho_v}{\partial T} gradT \quad (2)$$

where W is moisture content, P_c is capillary pressure, T is temperature, K_w is water permeability, K_{rw} is water relative permeability, μ_w is viscosity of water, f_{res} is gas resistant factor (tortuosity) according to Milligton model [2], D_{va} is water vapor diffusion coefficient, ρ_v is water vapor density.

According to the Kelvin's law, the capillary pressure is:

$$P_c = -\rho_e \frac{RT}{M_v} \ln\varphi \quad (3)$$

$$\rho_v = \frac{M_v}{RT} P_v = \frac{M_v}{RT} \varphi . P_{vs} \quad (4)$$

Supposing that the relative humidity varies slightly according to the temperature, we can write:

$$\left. \begin{array}{c} K_{vW} = -f_{res} D_{va} \frac{M_v}{RT} P_{vs} \frac{\partial \varphi(W)_T}{\partial W} \\ \\ K_{vT} = -\frac{M_v}{R} \varphi(W)_T \frac{\partial (P_{vs}/T)}{\partial T} \end{array} \right\} \quad (5)$$

In the equation (5, the gradient $\frac{\partial \varphi(W)_T}{\partial W}$ is represented by the curves sorption-desorption. In this work, these curves are experimentally determined (see the next section).

By applying mass balance law, one thus obtains:

$$\underbrace{\frac{\partial(\rho_w W)}{\partial t}}_{water\ temporal\ derivative} = -div\left(\underbrace{J_w}_{water\ flux} + \underbrace{J_v}_{vapor\ flux} \right) \quad (6)$$

2.2. Heat transfer

In the framework of this work, we neglected both the heat released during the hydration and the heat coming from the phase shift liquid-vapor. Indeed, the heat emission caused by the hydration of cement materials is significant only in the few first hours of hydration when cracking is neglected. Consequently, for a cement material studied for an extended period of time, this phenomenon is negligible. As for the phase change liquid-gas, the transfer of heat induced by the gas flux is supposed to be null. Moreover, the flux of the fluid within a cement based material which has a fine porosity is proved very slow. This involves that the contribution of the heat flow generated by the convection of the liquid becomes is also negligible. Because of the previous reasons, the heat transfer is purely induced by conduction. Thus, the equation of heat transport can be written as [3–5]:

$$\rho_c C_{pc} \frac{\partial T}{\partial t} - div(\lambda_{eff} gradT) = 0 \quad (7)$$

where ρ_c and C_{pc} are respectively, the concrete density and its heat capacity. To quantify the effective conductivity λ_{eff}, we are based on the model proposed by [3–5].

$$\lambda_{eff} = \lambda_{eff}^{ref} \left(0.244 \left(\frac{W}{\in_p} - 1\right) + 1 \right) (0.0015(T - T_{ref}) + 1) \quad (8)$$

With:

λ_{eff}^{ref}: Effective thermal conductivity of concrete measured in reference condition.
T: Material temperature.
T_{ref}: Temperature of reference.

In our research, we study a range of temperatures which are not enormously different from the temperature of reference, therefore product 0.0015 $(T - T_{ref})$ is very small compared to 1, then, the relation (8) is reduced to: