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Experimental investigation of solute transport in unsaturated cement pastes

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ABSTRACT

This article is dedicated to the development of a method for acquiring experimental data on ionic diffusion in partially saturated cement-based materials. A modified “half-cell” method is adopted in order to introduce the diffusing solute without disturbing the initial water content of the material. After a certain diffusion time (5 to 10 months), the concentration profiles of the tracer within the samples are measured by elemental mapping using the Laser Induced Breakdown Spectroscopy technique (LIBS). Analyses of the diffusion profiles obtained show a net decrease of the liquid-phase diffusivity with desaturation of the material, in accordance with the results in the literature. The innovation provided by this study consists in taking into account the adsorption of the tracer (Li) in the analytical processing of the diffusion profiles. This adsorption was quantified by measuring the interaction constant.

1. Introduction

In sustainability studies dealing with cement-based materials, degradation kinetics are mostly controlled by material transport mechanisms (leaching, carbonation, corrosion, etc.) [1–5]. On the other hand, this degradation can alter the microstructure of the material and thus have a retroactive effect on the transport kinetics. Thus, predicting the kinetics of this degradation in order to ensure the strength of the structure over the long term, one must be able to predict the material's containment parameters on the basis of its intrinsic properties and its environment.

When a degradation mechanism is governed by a gas-phase transport process (CO_2 for atmospheric carbonation, for example), the desaturation of the pores in the cementitious environment can accelerate this transport and thus become detrimental to the integrity of the reinforced material. A gas diffusion law, based on the degree of saturation of the material, is therefore necessary. However, other evolution phenomena of the material involve ionic diffusion in unsaturated conditions, such as the migration of chlorides and radionuclides, as well as atmospheric carbonation that can be controlled by the diffusion of calcium. The saturation state must be considered when developing these transport laws in order to improve the reliability of the tools used to predict these phenomena.

Until now, the effect of saturation on ionic diffusion has been introduced via a few empirical models based on experimental data. These laws are often associated with transport phenomena in unsaturated soils where the complex and multi-scale character of the concrete's porosity has not often been taken into account. In addition, the validation of this type of law has always encountered difficulties in directly measuring the diffusion in the liquid phase partially saturating the pores of a cement-based material.

2. Available testing methods

Two types of tests were identified in diffusion studies in partially saturated soils: the measurement of electric conductivity (EC method) and the “half-cell” method. The first is an indirect method which has the advantage of having access to the effective diffusion coefficient of an unsaturated material without disturbing its original water content [6–8]. However, precautions must be taken in order to minimise the influence of the resistance of the material/electrode contact on the material's resistivity measurement. The second consists in placing two samples of the material (source and target) into contact with one another in a sealed cell [7,9]. The source sample is uniformly predoped with tracer, while the target sample is tracer free. This method seems to give satisfactory results provided that perfect contact is maintained between the two elements. The diffusion coefficients identified by this method are consistent with values derived from the EC method.

As far as the empirical models identified from these experiments are concerned, it is interesting to note that for the majority of the soils tested, the diffusion coefficient appears to change with the square of the degree of saturation [8]. The generalised Archie's law appears to adequately describe the diffusion in unsaturated soils of different types and over a wide range of porosity. The existence of a critical saturation

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threshold from which the diffusion stops appears to be linked to the discontinuity of the liquid phase in the porous network. It appeared that this critical threshold essentially depends on the textural properties of the material. An empirical law was identified linking this threshold parameter to the specific surface of the material [9].

There are not many diffusion tests in unsaturated cement-based materials in the literature. Still, the works of Francy and François [10] can be cited which proposed a law describing the evolution of the diffusion coefficient by correlating the variation of the electrical conductivity, determined by impedance spectrometry, and water saturation. Four CEM I based mortars were tested. The experimental results of the diffusion coefficient indicate a saturation threshold near 55%.

In Climent and De Vera's approach [11,12], the challenge was to introduce chloride ions into the porosity of the partially saturated concrete without disturbing its water content. The procedure consisted in exposing the samples to PVC combustion gases. The diffusion profiles in the thickness of the samples were measured after 6 months in 1 mm increments. A review of experimental results showed a linear trend between the diffusivity and the degree of saturation as well as the existence of a saturation threshold of near 30%.

Chloride diffusivity measurements in a partially saturated mortar were conducted by Nielsen and Geiker [13]. In this test, the chlorides were introduced by temporal immersion in a NaCl solution followed by rapid drying until the initial mass was recovered. The diffusion profiles in the materials were measured after 60 days by successive scraping with a pitch of 2 mm. The results were compared to an empirical law proposed by Saetta and Scotta [14] concerning the evolution of the chloride diffusion coefficient with the relative humidity, inspired by the law proposed by Bazant and Najjar [15] for hygric diffusivity.

Diffusion of ions in cement-based materials is strongly influenced by the evolution of the saturation in the pores. Diffusive transport in the liquid phase is limited in unsaturated concrete. This phenomenon may be related to a reduced amount of available space for diffusion to occur, to an increase of the tortuosity and/or to a discontinuity of the liquid phase in the elementary phases contributing to the transport (capillary porosity, internal and external C–S–H).

Before proposing an integrated model in the chemistry/transport/mechanical coupled codes, it is essential to understand the effects of saturation on the physico-chemical processes involved during diffusive transport. In order to address these requirements, this paper is dedicated to the development of a method for acquiring experimental data on ionic diffusion in partially saturated cement-based materials. After a reminder of the theoretical aspects involved and a description of the experimental setup, absorption and diffusion tests in saturated and unsaturated conditions are presented.

3. Theory

In saturated conditions, solute diffusion within cement-based materials is entirely described by the mass balance equation. By assuming the validity of the Fick's 1st law and by neglecting the effect of other ions, the mass balance equation can be given by:

$$\frac{\partial C_{tot}}{\partial t} = D_e \frac{\partial^2 C_f}{\partial x^2} \tag{1}$$

where,

$$C_{tot} = \phi C_f + (1-\phi)\rho_s C_b \tag{2}$$

C_{tot}	total amount of diffusing solute per volume of material
C_f	amount of free diffusing solute per volume of liquid solution
C_b	amount of bound solute per mass of solid phase
D_e	effective diffusion coefficient of the material
ϕ	the material porosity
ρ_s	the solid phase density.

By assuming linear and reversible interaction of solute with solid matrix, we can write:

$$K_d = \frac{\partial C_b}{\partial C_f}. \tag{3}$$

And then, we obtain:

$$\frac{\partial C_f}{\partial t} = D_a \frac{\partial^2 C_f}{\partial x^2} \tag{4}$$

where the apparent diffusion coefficient is expressed as:

$$D_a = \frac{D_e}{\phi + (1-\phi)\rho_s K_d}. \tag{5}$$

As described in Fig. 1b, an adsorbed liquid film is considered in partially saturated conditions. From this assumption, the amount of bound solute is not affected but the free solute quantity is weighted by a degree of saturation as:

$$\frac{\partial C_f}{\partial t} = \frac{D_e}{\phi S_l + (1-\phi)\rho_s K_d} \frac{\partial^2 C_f}{\partial x^2}. \tag{6}$$

4. Experimental

4.1. The half-cell diffusion test

In the diffusion experiments conducted in an unsaturated porous medium, it is often difficult to introduce the diffusing solute without disturbing the original water content of the material (degree of saturation in the pores). To overcome this obstacle, the half-cell method is adopted. The principle of this simple method consists in placing two samples of the material (source and target) into contact with one another in a sealed cell, Fig. 2. The source sample is uniformly pre-doped with tracer, while the target sample is tracer free. Bonding with fresh cement paste improves the continuity of the porous network between the source and the target during the diffusion test.

In these diffusion cells, 1 cm thick samples (4 × 4 cm cross-section) are tested. After a certain diffusion time (5 to 10 months), the concentration profiles of the tracer in the thickness of the two samples are measured by elemental mapping. The Laser Induced Breakdown Spectroscopy technique (LIBS) uses laser ablation to evaporate a quantity of material (nanogram) located at various points in the depth of the material. The chemical composition of this evaporated material (plasma) is analysed on line by optical spectroscopy. A description of this analysis technique is provided in Appendix A.

4.2. Materials

Within the scope of this experimental campaign, a CEM I (OPC) cement paste was produced with a w/c ratio of 0.4. The cement pastes are poured into 4 × 4 × 16 cm moulds. After being released from the mould, they are kept in two cure solutions that are oversaturated in $Ca(OH)_2$ and doped in sodium (47 mmol/l) and potassium (452 mmol/l). These concentrations were identified from the composition of an extracted pore solution of a similar mature cement paste. From these specimens, 1 cm thick samples (4 × 4 cm cross-section) are cut with a wire saw under water.

After 15 days, the "source" samples are returned to their cure solution with an additional 100 mmol/l of lithium ($LiNO_3$). These samples were kept in their Li-doped cure solution for three months. The "target" samples were kept in their lithium-free cure solutions for the same period of time.

Lithium was chosen as a tracer to measure the effective diffusivity of the materials studied owing to its low interaction with the cement matrix [16]. For the doped samples, during the manufacture of the