Effect of the pore size of cement based materials on ionic transport

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HIGHLIGHTS

- A model accounting for the EDL effect on the ions concentration in pores is proposed.
- The model is based on the Poisson and Debye-Hückel equations in migration.
- The average concentrations in the pore are modified, together with the ionic fluxes.

ARTICLE INFO

ABSTRACT

The study of the electrochemical behavior of the cement-based materials/pore solution interface is an important topic in order to understand the transport of ionic species. It is also relevant for the purpose of interpreting the experimental results obtained in ionic transport tests (natural diffusion, or migration). The inherent issue in the interpretation of experimental results from ionic transport tests is the link between transport phenomena occurring at pore scale and the access to only macroscopic data and results. Indeed, the ionic concentrations of the pore solution are necessary data for the application of the Nernst-Planck equation.

We demonstrate here that the pore size has impact on the results on the ionic concentrations distribution at macroscopic scale. Consequently the electrical conductivity is also modified. This works helps to understand why the results of migration tests may lead to wrong interpretations in terms of material conductivity and ionic diffusivity.

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1. Introduction

The study of the electrochemical behavior of the cement-based materials/pore solution interface is an important topic in order to understand the transport of ionic species. It is also relevant for the purpose of interpreting the experimental results obtained in ionic transport tests (natural diffusion, or migration). Accelerated tests by means of an external electrical field provide the effective diffusion coefficient of porous material with a good accuracy as long as the boundary conditions are properly controlled [1–9].

For example, we demonstrated recently that Electrochemistry Impedance Spectroscopy (EIS) associated to an equivalent electrical circuit accounting for the material microstructure is a fast and accurate technique to assess the effective diffusion coefficient of concrete [1]. Moreover the experimental test developed in our group allowed to determine the diffusivity when the porous sample is partially saturated [10].

When it comes to diffusion, the data are available at macroscopic level: they are the species concentrations in the two reservoirs sandwiching the tested sample, together with the ionic composition of the saturation solution, in the case of a natural diffusion test. When electrical methods are used, the external potential difference is also measured in a DC test or the impedance corresponding to the range of imposed frequencies in an AC test (EIS).

Porous materials are made of a solid phase and a pore network which size distribution may vary from nanometers to micrometers. This is particularly true when it comes to cement-based materials, which possess in addition a pore surface electrical charge varying with the ionic composition of the pore solution and its pH [11–13]. The excess charge of the pore walls is counterbalanced by ionic species of opposite sign present in the pore solution, the counter-ions. As a result, the concentration of ions in the vicinity of the pore walls is different from the one in the bulk solution – away from the walls. The counter-ions are located in a region called the Electrical Double Layer (EDL). For more details on the EDL we refer to the books of [14,15].

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The inherent issue in the interpretation of experimental results from ionic transport tests is the link between transport phenomena occurring at pore scale and the access to only macroscopic data and results. This is important as migration tests offer also the possibility to measure indirectly the pore connectivity.

In this paper we are interested in the effect of the pore size on the ionic distribution and the corresponding species fluxes at pore scale in various conditions: (i) the pore is placed between 2 reservoirs at constant concentrations, (ii) an additional external potential difference is applied. For the sake of clarity, the example of the pore solution of a cement paste with mineral additions (type V cement) will be taken.

2. Model

We start our analysis by considering one single cylindrical channel of length L and diameter d placed between two reservoirs. The channel and the 2 reservoirs are filled with the same electrolyte solution made of Na^+, K^+ and OH^-. Here $d \ll L$ and the channel is considered to represent a pore. The pore wall is charged with a uniform electrical surface potential ψ_s. Attached to this configuration is a cylindrical frame (O, r, x), where $r = 0$, $0 \leqslant x \leqslant L$, corresponds to the longitudinal axis of the pore. Note the angular symmetry along (Ox). Fig. 1 shows the main geometrical features of the problem.

The electrical potential $\psi' = \psi - \psi(O)$, which depends on the distance from the wall only, is given by the Poisson equation [14]:

$$\nabla \psi' = -\frac{\rho}{\varepsilon_s} \tag{1}$$

where ε_s is the solution permittivity, and ρ is the charge density written as:

$$\rho = F \sum_i z_i c_i \tag{2}$$

where F is the Faraday constant, z is the charge number and c is the concentration of the species i. Here $\psi(O)$ is the electrical potential along the axis, $r = 0$.

The combination of Eqs. (1) and (2) leads to:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi'}{\partial r} \right) = -\frac{F}{\varepsilon_s} \sum_i z_i c_i \tag{3}$$

The Boltzmann distribution [15] expresses the spatial concentration distribution:

$$c_i(r,x) = c_i(0,x) \exp \left(-\frac{z_i F}{RT} \psi' \right) \tag{4}$$

where R is the gas constant and T is the temperature.

As we assumed that the channel is filled with a solution identical to the reservoirs solutions, $c_i(0,x) = c_i(0)$ and by the same token the concentration in Eq. (4) depends only on the radius r.

Next, following [16], the concentration along the cylinder axis is determined by writing that:

$$c_i(O) = c_i^{res} \exp \left[-\frac{z_i F}{RT} (\psi(0) - \psi^{res}) \right] \tag{5}$$

where ψ^{res} is the electrical potential in the reservoir, null at this stage.

Note that Eqs. (4) and (5) are expressions that cover the case when the Electrical Double Layers (EDL) overlap. If the pore diameter is large enough then $\psi(0) = 0$ and the concentration along the pore axis is given by $c_i(0) = c_i^{res}$.

We have:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi'}{\partial r} \right) = -\frac{F}{\varepsilon_s} \sum_i z_i c_i(0) \exp \left(-\frac{z_i F}{RT} \psi'(r) \right) \tag{6}$$

In order to solve Eq. (6) we proceed in 2 steps. First of all we start by considering that the solution is not anymore made of sodium, potassium and hydroxide but simply binary and symmetric (1:1), which means of anions and cations with $|z_i| = 1$. Then we apply the Debye-Hückel approximation. We obtain:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \psi'}{\partial r} \right) = \kappa^2 \psi'(r) \tag{7}$$

With

$$\kappa^2 = \frac{2F^2}{\varepsilon_s RT} \sum_i \frac{1}{2} z_i^2 c_i(0) \tag{8}$$

and κ^{-1} is the Debye length. Note that $\sum_i \frac{1}{2} z_i^2 c_i(0)$ is also termed as the ionic strength.

The boundary conditions are:

$$r = 0, \qquad \frac{\partial \psi'}{\partial r} = 0 \tag{9}$$

$$r = \frac{d}{2}, \psi' = \psi'_s = \psi_s - \psi \tag{10}$$

The solution of Eq. (7) together with the boundary conditions Eqs. (9) and (10) is [17]:

$$\psi'(r) = \psi'_s \frac{I_0(\kappa r)}{I_0(\kappa d/2)} \tag{11}$$

where I_0 is the zero order modified Bessel function of the first kind.

Eq. (11) depends on the value of the Debye length which itself is given by the concentration along the pore axis and therefore the electrical potential at the axis $\psi(0)$. $\psi(0)$ is null when the EDL is small but remains unknown in case of overlap. Therefore we implemented a numerical procedure consisting in assuming an initial value for $\psi(0)$, solving Eqs. (9)–(11), comparing the new value $\psi(0)$ to the initial one and changing it until the 2 match.

Once the radial electrical potential profile is obtained, we determine the ionic concentration by distributing the cations to Na^+ and K^+ as $c_{Na^+}^{res}$ and $c_{K^+}^{res}$ are known. Because we are interested ultimately in cement-based materials with small size pores, we chose a pore solution composition corresponding to the one of a type-V cement paste as analyzed in [1]: $c_{Na^+}^{res} = 71$, $c_{K^+}^{res} = 174$ mol/m³, and

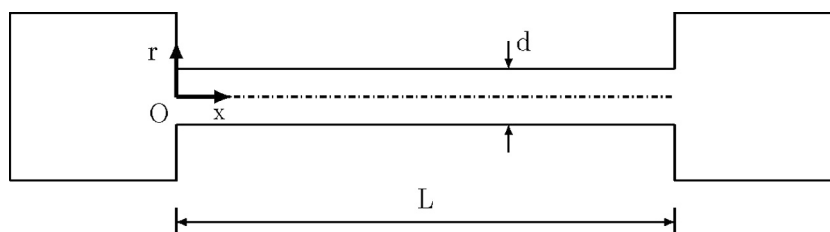**Fig. 1.** Cylindrical pore of length L and diameter d between 2 reservoirs.