Determination of the macroscopic chloride diffusivity in cementitious by porous materials coupling periodic homogenization of Nernst-Planck equation with experimental protocol

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ABSTRACT

In this paper, we propose a macroscopic migration model for cementitious porous media obtained from periodic homogenization technique. The dimensional analysis of Nernst-Planck equation leads to dimensionless numbers characterizing the problem. According to the order of magnitude of the dimensionless numbers, the homogenization of Nernst-Planck equation leads at the leading order to a macroscopic model where several rates can be coupled or not. For a large applied electrical field accelerating the transfer of ionic species, we obtain a macroscopic model only involving migration. A simple experimental procedure of measurement of the homogenized chlorides diffusivity is then proposed for cement-based materials.

Keywords: Cement-based materials; Chloride; Electrodiffusion; Periodic homogenization; Diffusion coefficient

1. INTRODUCTION

Reinforced concrete structures are designed for long time duration, from some years for usual structures to several centuries for particular structures such as the Channel tunnel. In case of radioactive wastes, the durability needed could reach several thousands of years. The structure durability is mainly affected by the attacks of the environmental aggressive agents, such as chlorides, whose penetration within the material induces either the reinforced steel corrosion or cracking and mineralogical modifications. Thus to predict the durability of concrete structures, it is necessary to have macroscopic models characterizing the diffusion of ionic species in cementitious porous materials.

In this paper we propose a macroscopic migration model deduced by periodic homogenization from Nernst-Planck equation, which leads to a simple procedure of measurement of the homogenized diffusion coefficient for cement-based materials. The approach proposed is based on the dimensional analysis of Nernst-Planck equation which naturally lets appear

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non-dimensional numbers characterizing the diffusion and migration of ionic species in saturated porous materials. Then the order of magnitude of these dimensionless numbers are determined from the experimental data of the electrodiffusion test described in section 5. Once reduced to a one scale-problem, the asymptotic expansion of Nernst-Planck equation leads to the searched homogenized macroscopic model. Moreover, we obtain explicitly an expression of the homogenized diffusion tensor D_k^{hom} . This way, we are certain that for the experimental data chosen (imposed electrical field, concentrations, mean pore diameter), at the leading order the mechanism governing the transport is that given by the asymptotic expansion of the Nernst-Planck equation.

In this paper, we focus on the case of an important applied electrical field corresponding to the experimental protocol of section 5. The homogenization procedure is developed at the scale of capillary porosity, whose characteristic length is given by mercury intrusion porosimetry results for the cement-based material considered. At this scale of porosity, which is larger than Debye's length, the double layer effects can be neglected. Then the macroscopic homogenized model obtained is a pure migration one. Moreover, the proposed approach matches also with a simple experimental protocol of measurement the homogenized diffusion coefficient for cement-based materials.

Periodic homogenization based on the double scale asymptotic expansions analysis has already been developed for transport laws in porous media, for classical Fick diffusion or coupled migration-diffusion problems [7] [8] [17]. It has been also extended to a coupling with electrical potential gradients in [6] [12] [13], using quasi-static Maxwell and Navier-Stokes equations [6], or an alternative microscale bulk formulation for expansive clays [12] [13]. However such a coupling between periodic homogenization of Nernst-Planck equation and experimental results is new and does not exist in the literature. This constitutes the main originality of the approach proposed in this paper.

2. THEORETICAL BACKGROUND OF MULTI-SPECIES IONIC TRANSPORT

2.1. DESCRIPTION OF THE PERIODIC MICROSTRUCTURE

Let us consider at the macroscopic scale that the medium studied (a cement or mortar sample) occupies the domain $\mathcal{S}^*$ of the three-dimensional space IR^3. At the macroscopic level, a current point of $\mathcal{S}^*$ will be noted $x^* = (x^*_1, x^*_2, x^*_3)$.

We assumed that the medium $\mathcal{S}^*$ has a periodic microstructure, or equivalently is constituted of the periodic repetition of an elementary cell $\Omega^* = \Omega^*_f \cup \Omega^*_s$ composed of a fuid phase Ω^*_f and of a solid phase Ω^*_s. The boundary Γ^* of Ω^*_f is composed of the inner boundary Γ^*_{fs} between the fluid and the solid phases, and of the part Γ^*_f between the fluid phases of two different cells (see Fig. 1). At the microscopic level, a current point of the elementary cell Ω^* is noted $y^* = (y^*_1, y^*_2, y^*_3)$.

In addition, the size l of the elementary cell Ω^* is assumed to be very small with respect to the dimension L of the material. This is a condition of the homogenizability of the problem. Thus the aspect ratio ε satisifies

$$\varepsilon = \frac{l}{L} < < 1$$

Moreover, in what follows we assume that all the fields involved and the associated boundary conditions are periodical with respect to the variable y^* . As a consequence, their derivatives are also periodical with the same period (the size l of the elementary cell). This assumption of periodicity of the field involved is classical [17] and is necessary for the periodic homogenization procedure to be consistent.

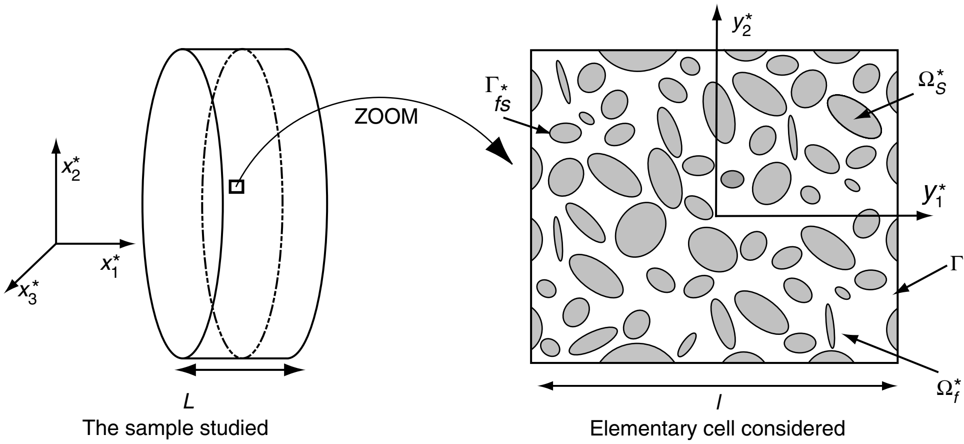

Figure 1 Modelling of the material heterogeneity by a periodic microstructure.

2.2. THE IONIC DIFFUSION IN THE LIQUID PHASE

In this paper we study the heterogeneous saturated porous materials whose microstructure contains two phases : a solid phase of aggregates and cement paste and a liquid phase; i.e the pore solution. The chemical interactions between the liquid and the solid phases, and the electrocapillary adsorption at the liquid-solid interface, which constitutes the electrical double layer, are neglected. The convection of the fluid in the fluid domain is also neglected.

In what follows, we index by a star (*) all dimensional variables. So that: $grad^*$, div^* and Δ^* will denote respectively the three-dimensional gradient, divergence and Laplacian with respect to the dimensional variables. *grad*, *div* and Δ will denote respectively the three-dimensional gradient, divergence and Laplacian with respect to non-dimensional variables.

The diffusion in the fluid phase is generally described by Nernst-Planck equation which writes [3][16]:

$$\frac{\partial^* C_k^*}{\partial t^*} + div^* \left(-D_k^* grad C_k^* - \frac{F}{RT} D_k^* grad^* \Psi^* Z_k C_k^* \right) = 0 \quad in \quad \Omega_f^* \tag{1}$$

where C_k^* denotes the concentration of the ionic species k of valence Z_k, D_k^* its molecular diffusion coefficient in the liquid phase[2], $E^* = -grad^* \Psi^*$ the electrical field in the solution, F and R respectively the Faraday and the ideal gas constant, T the temperature of the fluid. This equation is nothing else that the mass conservation for the ionic species of concentration C_k^* diffusing in the liquid phase. This equation must be completed with the associated boundary condition of non penetration of the ionic species in the solid phase $\mathcal{S}^*$:

$$\left(grad^* C_k^* \right) \cdot n = 0 \quad on \quad \Gamma_{sf}^* \tag{2}$$

where n denotes the external unit normal to the solid domain Ω_s^*.

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[2] For the sake of simplicity the diffusion tensor is assumed to be isotropic in the liquid phase, that is generally the case.

On the other hand equation (1) must be completed with Poisson equation:

$$\Delta^* \Psi^* = -\frac{\rho^*}{\varepsilon_\upsilon} \quad in \quad \Omega_f^* \tag{3}$$

which links the electrical potential Ψ^* to the electrical charge density

$$\rho^* = \sum_{k=1}^{N} F Z_k C_k^* \tag{4}$$

where ε_v denotes the dielectric constant of the medium. In cement based-materials the dielectric constant of the solid phase can be considered as negligible with respect to that of the liquid phase. In other terms, the solid phase is no conductive with respect to the fluid one. This writes in terms of boundary conditions:

$$grad^* \Psi^* \cdot n = 0 \quad on \quad \Gamma_{sf}^* \tag{5}$$

Let us notice that this problem written at the microscale level can be completed with boundary conditions at the macroscale level or equivalently at the scale of the material. In this paper, we consider that the concentrations C_k^* of the ionic species are given at the boundary $\partial \mathcal{S}^*$, and that the electrical field E^* is imposed on $\partial \mathcal{S}^*$. The last one, which will be used later, writes:

$$\frac{\partial \Psi^*}{\partial x^*} \cdot n = -E_{imp}^* \cdot n \quad on \quad \partial S^* \tag{6}$$

where E_{imp}^* denotes the imposed electrical field.

To finish, let us establish the following natural compatibility condition for the Neumann problem (3)-(5). Integrating equation (3) upon the fluid domain Ω^*_f we get:

$$\int_{\Omega_f^*} \Delta^* \Psi^* d\Omega^* = -\int_{\Omega_f^*} \frac{\rho^*}{\varepsilon_v} d\Omega^*$$

Using the divergence theorem (Stokes formulae) for the left member, and the boundary conditions (5), we get:

$$\int_{\Gamma_f^*} grad^* \psi^* \cdot n d\Gamma^* = -\int_{\Omega_f^*} \frac{\rho^*}{\varepsilon_v} d\Omega^*$$

where Γ^*_f denotes the fluid part of the boundary of Ω_f. Using the periodicity condition on ψ^*, the left member disappears and we obtain the compatibility condition:

$$\int_{\Omega_f^*} \rho^* d\Omega^* = 0 \tag{7}$$

which will be useful later in the calculations. This condition means physically that the electroneutrality must be satisfied in average on Ω_f^*, but not necessary locally.

2.3. DIMENSIONAL ANALYSIS OF EQUATIONS

Following the approach of [7] [10] [11], let us define the following dimensionless physical data and dimensionless unknowns of the problem:

$$y = \frac{y^*}{l}, \quad x = \frac{x^*}{L}, \quad t = \frac{t^*}{t_r}, \quad C_k = \frac{C_k^*}{C_r}, \quad D_k = \frac{D_k^*}{D_r}, \quad \Psi = \frac{\Psi^*}{\Psi_r} \tag{8}$$

where the variables indexed by r are the reference ones. The new variables which appear (without a star) are dimensionless. Introducing the dimensionless variables previously defined in equations (1) and (3), we obtain a new dimensionless problem posed in Ω_f:

$$\mathcal{T}\frac{\partial C_k}{\partial t} + div\left(-D_k gradC_k - \mathcal{R}\ D_k grad\Psi Z_k C_k\right) = 0 \ \ in \ \ \Omega_f \tag{9}$$

$$\mathcal{A}\ \Delta\Psi = -\rho \ \ in \ \ \Omega_f \tag{10}$$

with the associated boundary conditions:

$$gradC_k \cdot n = 0 \ \ on \ \ \Gamma_{sf} \tag{11}$$

$$grad\Psi \cdot n = 0 \ \ on \ \ \Gamma_{sf} \tag{12}$$

Hence, the dimensional analysis of Nernst-Planck and Poisson equations naturally leads to dimensionless numbers characterizing the diffusion-migration problem:

$$\mathcal{T} = \frac{l^2}{D_r t_r}, \quad \mathcal{R} = \frac{\Psi_r F}{RT}, \quad \mathcal{A} = \frac{\Psi_r \varepsilon_v}{F l^2 C_r}$$

i) The dimensionless number $\mathcal{T} = \frac{l^2}{D_r t_r}$ represents classically the ratio of the characteristic time $\frac{l^2}{D_r}$ of molecular diffusion at the microscale to the characteristic time at the macroscale t_r. It is a small parameter and a given data of the problem.

ii) The dimensionless number $\mathcal{R} = \frac{\Psi_r F}{RT}$ is the product of the electrical potential with the constant $\frac{F}{RT}$ which depends only on the temperature. Thus $\mathcal{R}$ depends directly on the applied electrical potential. It can take important values.

iii) Finally, the dimensionless number $\mathcal{A} = \frac{\Psi_r \varepsilon_v}{F l^2 C_r}$ is not easy to interpret. It depends on the applied electrical potential and on the concentrations of the ionic species involved in the diffusion-migration phenomenon.

To finish, writing the boundary condition (6) in its non-dimensional form, we get:

$$grad\psi \cdot n = -E_{imp} \cdot n \quad on \quad \partial S \tag{13}$$

whereas the compatibility condition (7) becomes:

$$\int_{\Omega_f} \rho d\Omega = 0 \tag{14}$$

3. ASYMPTOTIC EXPANSION OF EQUATIONS

To obtain a one-scale problem, $\varepsilon = \frac{l}{L}$ is chosen as the reference perturbation parameter of the problem and the other dimensionless numbers are linked to the powers of ε. This will be done using the experiment data of section 5 and the results of [3] [9]. First, for the sample considered we have $L = 10^{-2}m$. Moreover, according to the results obtained from mercury intrusion porosimetry (see Fig. 2) for the cement based-material considered, the mean pore radii diameter is of the order of $0,1\mu m$.

In order the homogenization process to be consistent, we consider a characteristic length l of the elementary cell of the order of $l = 10\mu m$. So that the separation of scales is verified and we have:

$$\varepsilon = \frac{l}{L} = 10^{-3}$$

This choice of the elementary cell size, based on mercury intrusion porosimetry tests, leads to homogenize Nernst-Planck equations (or equivalently the transfer properties of the

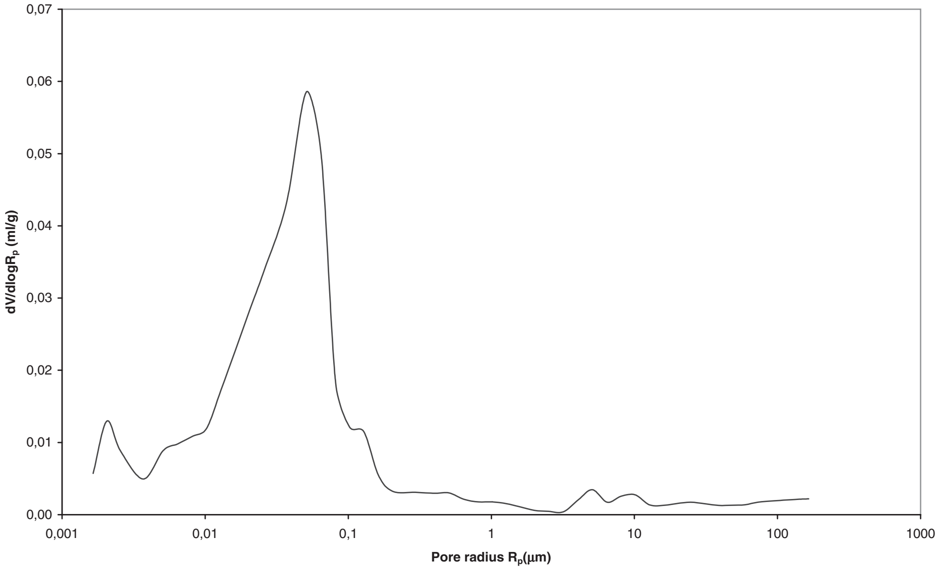

Figure 2 The mercury intrusion porosimetry results.

cement-based materials considered) at the scale of capillary porosity. So that the characteristic length of the cell, much larger than Debye's length, justifies the neglecting of the electrical double layer.

On the other hand, for the concentration $C_r = 0.5 mol/l$ of the ionic species involved in the process studied, whose diffusion coefficient in infinite dilution in water at 25°C is around $D_r = 10^{-9} m^2 s^{-1}$, and according to the value of $\varepsilon_v = 5.10^{-11} F/m$ in the pore solution, we find that $\mathcal{A} = O(\varepsilon^3)$. Finally, for an important electrical field $E^* = 300 V/m$ accelerating the diffusion process, we have $\Psi_r = LE_r = 3V$ and the characteristic time t_r of migration at the macroscale is a few minutes. So that we find that:

$$\mathcal{R} = O\left(\frac{1}{\varepsilon}\right) \quad and \quad \mathcal{T} = O(\varepsilon) \tag{15}$$

Finally, according to the experimental data used for the dimensional analysis, we will consider that:

$$\mathcal{R} = O\left(\frac{1}{\varepsilon}\right), \quad \mathcal{A} = O\left(\varepsilon^3\right) \quad and \quad \mathcal{T} = O(\varepsilon) \tag{16}$$

Replacing these values of the dimensionless numbers deduced from experimental analysis of the problem data in equation (9)-(11), we get:

$$\varepsilon \frac{\partial C_k}{\partial t} + div\left(-D_k gradC_k - \frac{1}{\varepsilon} D_k grad\Psi Z_k C_k\right) = 0 \quad in \quad \Omega_f \tag{17}$$

$$\varepsilon^3 \Delta\Psi = -\rho \quad in \quad \Omega_f \tag{18}$$

with the associated boundary conditions:

$$gradC_k \cdot n = 0 \quad on \quad \Gamma_{sf} \tag{19}$$

$$grad\Psi \cdot n = 0 \quad on \quad \Gamma_{sf} \tag{20}$$

Then the classical procedure of periodic homogenization [17] leads to search the unknowns C_k and Ψ of the problem as functions depending on the macroscopic variable x, on the microscopic variable y, and of the time t, considered as separate variables. This is justified because of the separation of scales ($\varepsilon << 1$). Moreover, the solution (C_k, Ψ) of the problem is postulated to admit a formal expansion with respect to ε [17]:

$$\begin{aligned} C_k &= C_k^0(x,t) + \varepsilon C_k^1(x,y,t) + \varepsilon^2 C_k^2(x,y,t) + \cdots \\ \Psi &= \Psi^0(x,t) + \varepsilon\Psi^1(x,y,t) + \varepsilon^2\Psi^2(x,y,t) + \cdots \end{aligned} \tag{21}$$

As the functions $C_k^i(x,y,t)$ and $\Psi^i(x,y,t)$ depend on the *independent* space variables x and y, the derivatives must be considered as composed derivative for several variable functions, where the separation of variables with respect to the scales L and $l = \varepsilon L$ must be taken into account. So that we have:

$$grad = \frac{\partial}{\partial y} + \varepsilon \frac{\partial}{\partial x}, \qquad \Delta = \Delta_y + 2\varepsilon \frac{\partial^2}{\partial x \partial y} + \varepsilon^2 \Delta_x$$

where Δ_y and Δ_x denote the Laplacian operator with respect to the variables y and x respectively.

Lemma 1

For an important applied electrical field and a weak convection velocity such as $\mathcal{R} = O\left(\frac{1}{\varepsilon}\right)$, $\mathcal{A} = O\left(\varepsilon^3\right)$ *and* $\mathcal{T} = O(\varepsilon)$, *the leading terms* C_k^i *of the expansion of* C_k *satisfy the electroneutrality assumption at the four first orders:*

$$\rho^0 = \sum_{k=1}^{N} Z_k C_k^0 \left(x,t\right) = 0, \quad and \quad \rho^i = \sum_{k=1}^{N} Z_k C_k^i \left(x,y,t\right) = 0, \quad for \ i = 1,2,3 \tag{22}$$

Proof :

The proof of this lemma stands straightforward from the dimensional analysis of Poisson equation and its asymptotic expansion. Indeed, replacing Ψ by its expansion (21) in equation (18), we obtain a chain of coupled problems $\mathcal{P}_0$, $\mathcal{P}_1$, $\mathcal{P}_2$.... corresponding to the cancellation of the factors of ε^0, ε^1, ε^2 ... respectively. Problem $\mathcal{P}_0$ writes:

$$\rho^0 = \sum_{k=1}^{N} Z_k C_k^0 \left(x,t\right) = 0$$

It is important to notice that this result is nothing else that the electroneutrality assumption at the first order which is generally assumed in the literature [14][18]. In the approach developed, it comes directly from the order of magnitude of the physical data of the problem. For the important imposed electrical field, we justify the electroneutrality at the leading order at the scale of the sample or of the material: $\rho^0(x,t) = 0$.

Moreover, going on the asymptotic expansion of Poisson equation, as ψ^0 does not depend on y, we get at order 1 to 3 corresponding to problems $\mathcal{P}_1$ to $\mathcal{P}_3$:

$$\rho^i = \sum_{k=1}^{N} Z_k C_k^i \left(x,y,t\right) = 0 \quad in \ \Omega_f \quad for \ i = 1,2,3$$

Therefore, according to the order of magnitude of the considered data of the problem, we obtain as a result that the electroneutrality is verified exactly in Ω_f at the first orders (from the leading order to order 3). At higher orders, the electroneutrality is only verified in average in Ω_f. Indeed, the asymptotic expansion of the dimensionless compatibility condition (14) leads to:

$$\int_{\Omega_f} \rho^i d\Omega, \quad for \ i \in \mathbb{N} \tag{23}$$

and in particular for $i \geq 4$.

Result 1

For an important imposed electrical field such as $\mathcal{R} = O\left(\frac{1}{\varepsilon}\right)$, $\mathcal{A} = O\left(\varepsilon^3\right)$, $\mathcal{T} = O(\varepsilon)$ *the leading terms* C_k^0 *of the expansion of* C_k *is solution of the macroscopic migration model:*

$$\varphi \frac{\partial C_k^0}{\partial t} - div_x\left(D_k^{hom} \frac{\partial \Psi^0}{\partial x} Z_k C_k^0\right) = 0 \tag{24}$$

where $\varphi = \dfrac{\left|\Omega_f\right|}{|\Omega|}$ *denotes the porosity of the material. The homogenized diffusion tensor* D_k^{hom} *is given by*

$$D_k^{hom} = \frac{1}{|\Omega|}\int_{\Omega_f} D_k\left(I + \overline{\frac{\partial \chi}{\partial y}}\right) d\Omega \tag{25}$$

where the vector $\chi(y)$ *is solution of the boundary problem*:

$$\begin{cases} div_y\left(D_k\left(I + \overline{\dfrac{\partial \chi}{\partial y}}\right)\right) = 0 \quad in \quad \Omega_f \\ D_k\left(I + \dfrac{\partial \chi}{\partial y}\right) \cdot n = 0 \quad on \quad \Gamma_{sf} \end{cases} \tag{26}$$

Moreover $E^0 = -\dfrac{\partial \Psi^0}{\partial x}$ *corresponds to the dimensionless electrical field applied at the boundary of the material.*

Proof: The proof of this result is split into three main steps from i) to iii)

i) *Determination of* Ψ^1

Let us keep on the asymptotic expansion of equations. The cancellation of the factor of ε^{-1} in Nernst-Planck equation leads to problem $\mathcal{P}_{-1}$ which is trivially satisfied as ψ^0 does not depend on y. In the same way, the cancellation of the factor of ε^0 leads to problem $\mathcal{P}_0$ which reduces to:

$$div_y\left(D_k\left(\frac{\partial \Psi^0}{\partial x} + \frac{\partial \Psi^1}{\partial y}\right) Z_k C_k^0\right) = 0 \;\; in \quad \Omega_f$$

with the boundary conditions (12) leading at order one to:

$$\left(\frac{\partial \Psi^0}{\partial x} + \frac{\partial \Psi^1}{\partial y}\right) \cdot n = 0 \quad on \quad \Gamma_{sf} \tag{27}$$

As C_k^0 does not depend on the variable y, we get equivalently:

$$div_y\left(D_k\left(\frac{\partial\Psi^0}{\partial x}+\frac{\partial\Psi^1}{\partial y}\right)\right)=0 \quad in \quad \Omega_f \tag{28}$$

In a classical way (see [17]), it can be proved that Ψ^1 can be written on the form:

$$\Psi^1=\overline{\Psi}^1(x,t)+\chi(y).\frac{\partial\Psi^0(x,t)}{\partial x} \quad in \quad \Omega_f \tag{29}$$

where χ is a periodic function of the variable y whose average on Ω_f is equal to zero. Then replacing expression (29) of Ψ^1 in equation (28), we obtain the following boundary problem characterizing χ:

$$\begin{cases} div_y\left(D_k\left(I+\overline{\frac{\partial\chi}{\partial y}}\right)\right)=0 \quad in \quad \Omega_f \\ D_k\left(I+\frac{\partial\chi}{\partial y}\right)\cdot n=0 \quad on \quad \Gamma_{sf} \end{cases} \tag{30}$$

where I denotes the identity of IR^3 and the overbar the transposition operator.

ii) The migration model

The cancellation of the factor of ε in Nernst-Planck equation leads to problem $\mathcal{P}_1$ which writes:

$$\begin{aligned}&\frac{\partial C_k^0}{\partial t}-div_x\left(D_k\left(\frac{\partial\Psi^0}{\partial x}+\frac{\partial\Psi^1}{\partial y}\right)Z_kC_k^0\right)-div_y\left(D_k\left(\frac{\partial C_k^0}{\partial x}+\frac{\partial C_k^1}{\partial y}\right)\right)\\&-div_y\left(D_k\left(\frac{\partial\Psi^1}{\partial x}+\frac{\partial\Psi^2}{\partial y}\right)Z_kC_k^0\right)-div_y\left(D_k\left(\frac{\partial\Psi^0}{\partial x}+\frac{\partial\Psi^1}{\partial y}\right)Z_kC_k^1\right)=0 \quad in \quad \Omega_f\end{aligned} \tag{31}$$

with the associated boundary conditions:

$$\left(\frac{\partial C_k^1}{\partial y}+\frac{\partial C_k^0}{\partial x}\right)\cdot n=0 \quad on \quad \Gamma_{sf} \tag{32}$$

On the other hand the cancellation of the factor of ε^5 in Poisson equation leads to:

$$\Delta_x\Psi^0+div_y\left(\frac{\partial\Psi^1}{\partial x}\right)+div_x\left(\frac{\partial\Psi^1}{\partial y}\right)+\Delta_y\Psi^2=-\rho^5 \quad in \quad \Omega_f \tag{33}$$

$$\left(\frac{\partial\Psi^1}{\partial x}+\frac{\partial\Psi^2}{\partial y}\right)\cdot n=0 \quad on \quad \Gamma_{sf} \tag{34}$$

where we have set:

$$\rho^5 = \sum_{k=1}^{N} Z_k C_k^5$$

Let us integrate equation (31) on the fluid domain Ω_f. Using the divergence theorem and boundary conditions (27), (32), (34), the periodicity conditions on the fields Ψ^i, C_k^i, we obtain:

$$\left|\Omega_f\right| \frac{\partial C_k^0}{\partial t} - \int_{\Omega_f} div_x \left(D_k \left(\frac{\partial \Psi^0}{\partial x} + \frac{\partial \Psi^1}{\partial y} \right) Z_k C_k^0 \right) d\Omega = 0 \quad in \quad \Omega_f$$

Finally, replacing Ψ^1 by its expression (29) we obtain the macroscopic migration equation:

$$\varphi \frac{\partial C_k^0}{\partial t} - div_x \left(D_k^{hom} \frac{\partial \Psi^0}{\partial x} Z_k C_k^0 \right) = 0$$

where $\varphi = \dfrac{\left|\Omega_f\right|}{|\Omega|}$ denotes the porosity of the material. The homogenized diffusion tensor D_k^{hom} is given by

$$D_k^{hom} = \frac{1}{|\Omega|} \int_{\Omega_f} D_k \left(I + \overline{\frac{\partial \chi}{\partial y}} \right) d\Omega \tag{35}$$

where $\chi(y)$ is solution of the boundary problem (30).

iii) Determination of Ψ^0

To finish, let us deduce the macroscopic equation verified by the potential Ψ^0 by integration of equation (33) upon Ω_f. Using the divergence theorem and boundary conditions (34), we get:

$$\int_{\Omega_f} \Delta_x \Psi^0 d\Omega + \int_{\Omega} div_x \left(\frac{\partial \Psi^1}{\partial y} \right) d\Omega = -\int_{\Omega_f} \rho^5 d\Omega$$

Replacing Ψ^1 by its expression (29), and according to the compatibility condition (23) at order 5 we obtain:

$$\int_{\Omega_f} div_x \left(\frac{\partial \Psi^0}{\partial x} + \overline{\frac{\partial \chi}{\partial y}} \cdot \frac{\partial \Psi^0}{\partial x} \right) d\Omega = 0$$

which can be written:

$$div_x \left(A \frac{\partial \Psi^0}{\partial x} \right) = 0$$

where we have set

$$A = \int_{\Omega_f} \left(I + \overline{\frac{\partial \chi}{\partial y}} \right) d\Omega \tag{36}$$

It can be proved from the definition (36) of A, where χ is defined by (26), that A is positive and definite positive if we assume that it is different from zero[3]. Finally we obtain the following Neumann problem for ψ^0:

$$\begin{cases} div_x \left(A \dfrac{\partial \Psi^0}{\partial x} \right) = 0 \quad in \quad \mathcal{S} \\ \dfrac{\partial \Psi^0}{\partial x} \cdot n = -E^n_{imp} \quad on \quad \Gamma_{sf} \end{cases} \tag{37}$$

where E^n_{imp} denotes the imposed electrical field on the boundary $\partial\mathcal{S}$ of the sample. The solution of this problem, defined up to an arbitrary constant, is given by:

$$\psi^0 = -E_{imp} \cdot x \tag{38}$$

where the dot denotes the scalar product of IR^3. Equivalently we have

$$E^0 = -\frac{\partial \Psi^0}{\partial x} = E_{imp}$$

which concludes the proof of result 1. Thus E^0 represents the imposed electrical field at the boundary of the sample.

4. BACK TO DIMENSIONAL VARIABLES

To go back to the initial dimensional variables, let us define

$$C_k^{*0} = C_r C_k^0, \quad \psi^{*0} = \psi_r \psi^0, \qquad D_k^{*hom} = D_r D_k^{hom}, \qquad \chi^* = l\chi \tag{39}$$

We have the following result:

<u>Result</u> 2

For an important imposed applied electrical field such as $\mathcal{R} = O\left(\frac{1}{\varepsilon}\right)$, $\mathcal{A} = O\left(\varepsilon^3\right)$, $\mathcal{T} = O\left(\varepsilon\right)$, *the leading terms* C_k^{*0} *is solution of the macroscopic migration model:*

$$\varphi \frac{\partial C_k^{*0}}{\partial t^*} - div_{x^*} \left(\frac{FZ_k}{RT} D_k^{*hom} \frac{\partial^* \Psi^{*0}}{\partial x^*} C_k^{*0} \right) = 0 \tag{40}$$

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[3] The case $A = 0$ would lead to $D^{hom} = 0$ which is not physically acceptable.

where the porosity is given by $\varphi = \frac{|\Omega_f|}{|\Omega|}$*. The homogenized dimensional diffusion tensor* $D_k^{*\,hom}$ *is given by*

$$D_k^{*hom} = \frac{1}{|\Omega^*|}\int_{\Omega_f^*} D_k^*\left(I + \overline{\frac{\partial^* \chi^*}{\partial y^*}}\right) d\Omega^* \tag{41}$$

where the vector $\chi^*(y^*)$ *is solution of the boundary problem:*

$$\begin{cases} div_{y^*}\left(D_k^*\left(I + \overline{\frac{\partial^* \chi^*}{\partial y^*}}\right)\right) = 0 \quad in \quad \Omega_f^* \\ D_k^*\left(I + \frac{\partial^* \chi^*}{\partial y^*}\right)\cdot n = 0 \quad on \quad \Gamma_{sf}^* \end{cases} \tag{42}$$

Moreover $E^{*0} = -\frac{\partial \Psi^{*0}}{\partial x^*}$ *corresponds to the dimensionless electrical field applied at the boundary of the material.*

Proof: Let us go back to the physical variables (39) in equations of result 1. Using (8), we obtain:

$$\frac{\varphi t_r}{C_r}\frac{\partial C_k^{*0}}{\partial t^*} - \frac{L^2}{D_r \psi_r C_r} div_{x*}\left(Z_k D_k^{*hom}\frac{\partial^* \Psi^{*0}}{\partial x^*} C_k^{*0}\right) = 0$$

or equivalently

$$\frac{\varphi \varepsilon^2}{\tau}\frac{\partial C_k^{*0}}{\partial t^*} - \frac{1}{\mathcal{R}} div_{x^*}\left(\frac{FZ_k}{RT} D_k^{*hom}\frac{\partial^* \Psi^{*0}}{\partial x^*} C_k^{*0}\right) = 0$$

Then using the order of magnitude of the dimensionless numbers given by (15), we have $\tau = \varepsilon$ and $\mathcal{R} = \frac{1}{\varepsilon}$, which leads to the dimensional equation (40). The end of the proof of the result does not contain any difficulty and is left to the reader.

5. APPLICATION TO THE EXPERIMENTAL MEASUREMENT OF D^{*hom}

Let us start from the dimensional migration model (40). The experimental determination of D^{*hom} can be done using a classical electrodiffusion test. It consists of a cell in which the sample tested is placed between two compartments (Fig. 3). The diffusion is accelerated by applying an electrical field of $\|E^{*0}\| = 300 V/m$. It is maintained constant between the sides of the sample by a four electrodes set-up. For cement-based materials, the test is based on a downstream dosage of chlorides. The migration test is carried out in two steps:

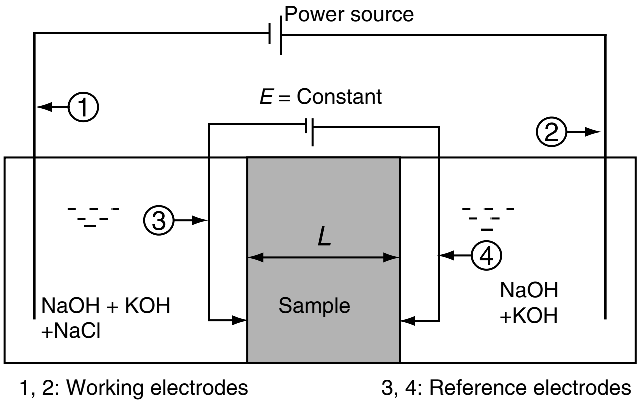

Figure 3 Schematic view of the electodiffusion cell.

(i) in a first step, the two compartments contain the same basic solution of NaOH and KOH to simulate the alkaline pore solution of usual cement-based materials. The electrical field is applied during this step in order to saturate the sample with this solution and to homogenize the cell solution with pore solution.

(ii) in a second step, NaCl is added to the upstream in a concentration of 0.5 mol/l and the same electrical field is applied. This concentration is maintained constant by regular renewals of the upstream solution. Measurements consist in the dosage according to time of the chloride concentration in the downstream compartment until obtaining the steady state. This later corresponds to a linear increasing with time of the cumulated chloride concentration in the downstream compartment[4].

The experiment is made on a mortar cylindrical sample of diameter 6.5 cm and thickness 1 cm. The cement used is of type CEMI-52.5 according to the European norm EN 197-1. The lateral surfaces of the sample are coated with resin so that the diffusion can be considered as one-directional in the thickness direction. The chloride concentration evolution according to time, in the downstream compartment, is plotted on figure 4. The gradient of the linear part of the curve gives the constant flux through the thickness at the steady state:

$$J^* = \frac{\Delta C_0^* V_a^*}{\Delta t^* A^*} \tag{43}$$

where V_a^* is the volume of the downstream compartment of the cell, A^* the sample surface submitted to ionic transfer and $\Delta C^*{}_0$ the variation of the chloride concentration measured during a period of time Δt^*.

On the other hand, as the experimental data (imposed electrical field, concentration of the chloride ions ...) are such as $\mathcal{R} = O\left(\frac{1}{\varepsilon}\right)$, $\mathcal{A} = O\left(\varepsilon^3\right)$ *and* $\mathcal{T} = O\left(\varepsilon\right)$, the results of the homogenization process developed in the first part of this paper ensure that, at the leading order, the flux of chlorides J^* in the steady state is given from (40) by:

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[4] For these measurements, a chloride selective electrode is used in combination with a reference electrode. The two electrodes are connected to a milli-voltmeter.

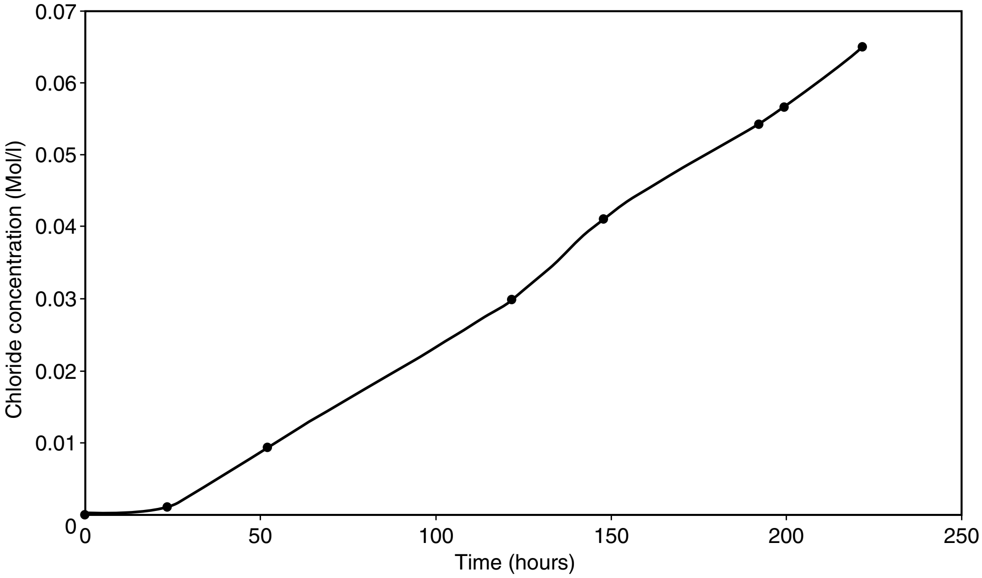

Figure 4 Evolution of the cummulative chloride concentration in the downstream compartment according to time.

$$J^* = \frac{\left|Z_{Cl^-}\right| F D_{exp}^{*hom} C_{Cl^-}^{0*} \left\|E^{*0}\right\|}{RT} \tag{44}$$

where $C^*_{Cl^-}$ denotes the initial chloride concentration in the upstream compartment. Then the experimental value of D^{*hom}_{exp} of the homogenized coefficient is deduced from (44):

$$D_{exp}^{*hom} = \frac{RT\ J^*}{\left|Z_{Cl^-}\right| F \left\|E^{*0}\right\| C_{Cl^-}^{0*}} \tag{45}$$

where the value of J^* is obtained experimentally. It is important to notice that, with such accelerated migration tests, the measure of J^* and then of D^{*hom}_{exp} is possible after a few hours that corresponds to the establishing of the steady state. In contrary, in natural diffusion, the establishing time of the steady state is several months, so that the experimental determination of D^{*hom}_{exp} is much longer.

The numerical application of equation (45) for the experiments carried out gives

$$D_{exp}^{*hom} = 3{,}6.10^{-12}\, m^2/s$$

for the mortar considered. Let us notice that comparison of the experimental value of D^{*hom}_{exp} to the theoretical value of D^{*hom} given by (41) is not an easy task. If the geometric description of the elementary cell is too simple (cylindrical pores infinite in one direction or even spheroidal inclusions), the value of D^{*hom} obtained is close to φD^* which is far from the experimental one. So that the computation of D^{*hom} must be done using a complex geometrical description of the elementary cell taking into account the tortuosity and constrictivity which contribute to slow down the transfer. However, this is out of the scope of the present paper. Moreover, the adsorption phenomena which occur at the interface between the solid phase and the liquid one within the material (called electrical double layer), must also be taken into account [3]. It has been neglected in this paper because of the homogenized procedure developed at the scale of capillary porosity.

6. CONCLUSION

The periodic homogenization of the Nernst-Planck equation leads to a macroscopic migration model at the leading order, valid for experimental data such as $\mathcal{R} = O\left(\frac{1}{\varepsilon}\right)$, $\mathcal{A} = O\left(\varepsilon^3\right)$ and $\mathcal{T} = O\left(\varepsilon\right)$. Moreover the procedure developed leads to a simple experimental procedure to measure the homogenized diffusion coefficient involved, based on electrodiffusion test which can be extended to any porous saturated materials. Once $D^{*\,hom}_{exp}$ determined experimentally, predictions of the diffusion at the material scale on very long times are possible.

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