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Describing ion diffusion mechanisms in cement-based materials using the homogenization technique

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Abstract

The application of the homogenization technique to the mathematical description of the diffusion mechanisms in saturated cement-based materials is discussed. According to this approach, the transport and mass conservation equations are first written at the microscopic scale to describe the movement of particles in the fluid phase of the material. These equations are then averaged over the entire volume of the material. An example of the application of the homogenization technique is given. The homogenization technique is used to describe the diffusion of ions in cement-based systems. The various equations are written to consider the charged nature of the ionic particles and the coupling between the various ionic fluxes. The numerous advantages of this technique for the modeling of mass transport mechanisms in cement-based materials are discussed.

Keywords: Homogenization; Representative elementary volume; Ionic diffusion; Nernst-Planck; Poisson

1. Introduction

Concrete structures are exposed to various types of aggression during their service life. Deterioration mechanisms generally involve the penetration of external ions into the cement system pore structure. This results in chemical and physical interaction with the binder solids, including leaching of chemical species. In many cases, these phenomena occur simultaneously. The durability of the material is therefore often directly controlled by its ability to act as an impervious barrier that can effectively impede, or at least slow down, the mass transport processes.

Although capillary absorption and permeation (i.e., the transport of a fluid under a pressure gradient) can in certain cases be of significant importance, numerous studies have clearly indicated that ions are mainly transported through the concrete pore structure and microcracks by a diffusion process [1–3]. This is why the mechanisms of diffusion in saturated cement-based materials have received considerable attention [4].

Literature review [4] has recently indicated that despite the relative agreement on the parameters that affect the ionic diffusion mechanisms in saturated cement systems (mixture characteristics, length, type of curing, etc.), a lack of consensus on how to characterize the diffusion properties of these materials exists. Some authors choose to consider the diffusion coefficient as an intrinsic characteristic of the overall material. Others prefer to treat it as a property of the liquid phase. Unfortunately, there appears to be no definitive agreement on the mathematical procedure to convert one coefficient into another.

An attempt to clarify the mathematical treatment of diffusion mechanisms in saturated cement systems is presented. The mass transport equations are derived using the homogenization technique. The fundamental assumptions implicit in the application of this technique lie in the theoretical treatment of the porous system. The later is considered as comprised of the sum of solid, liquid, and eventually gaseous phases. Although there can be exchanges of mass between them (through chemical reactions or any physical interaction phenomenon), each individual phase is treated as a distinct entity.

The first step of the homogenization technique consists of writing the transport and mass conservation equations at the microscopic scale. These equations are then averaged over the entire volume of the material. The various aspects of the averaging technique are well described in the text. The appli-

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cation of this approach to the description of ionic diffusion mechanisms in cement-based materials is discussed.

2. Description of the ionic diffusion mechanisms in the liquid phase

The application of the homogenization technique first requires writing the mass and transport equations at the microscopic scale. For the particular case of ion diffusion in saturated cement-based materials, the assumption that transport occurs predominantly in the liquid phase is required. The application of the mass conservation equation for an ionic species diffusing in the liquid phase yields Eq. (1):

$$\frac{\partial c_i}{\partial t} + \mathrm{div}(j_i) = 0 \tag{1}$$

where c_i is the concentration of the considered species in solution and j_i is the flux of the same species in the liquid phase. It should be emphasized that Eq. (1) has to be repeated for each and every ionic species present in solution. Also, no chemical reactions appear in this equation. At the pore scale, they are modeled by boundary conditions.

In order to reliably describe the flux of a given species, one has to account for the particularities of ionic diffusion mechanisms in liquids. Contrary to molecules, ions are charged particles. In addition to the viscous-drag force exerted by their environment, drifting ions will also be subjected to various electrical forces. For instance, the charged nature of the ionic particles is at the origin of various interactions between the drifting particles (ion/ion interactions and ion/solvent interactions). These so-called activity effects quickly become important as the concentrations of the various ions in solution increase. The electrical charge of the particles may also contribute to generate specific ion/solid interactions that can be both physical or chemical in nature. More information on these two phenomena can be found in previously published works [4,5].

Despite the relative importance of activity effects and ion/solid interaction phenomena, it is emphasized that the most important feature that distinguishes ion diffusion from molecular diffusion is the electrical coupling of the various ionic flows [4,6,7]. In an ionic solution, the local electroneutrality shall be preserved at any point. The conservation of electroneutrality requires that the flows of all diffusing species should be coupled. During the diffusion process, all ions are not drifting at the same speed. Some ions tend to diffuse at a higher rate. However, any excess charge transferred by the faster ions builds up a local electric field (called the diffusion potential), which slows down the faster ions, and reciprocally accelerates the slower ions.

It can be shown that the mechanisms of ionic diffusion in solution can be reliably described on the basis of Eq. (2) [4–6]:

$$j_i = -D_i^{\mu}\mathrm{grad}(c_i) - \frac{D_i^{\mu} z_i F}{RT} c_i \mathrm{grad}(\psi) - D_i^{\mu} c_i \mathrm{grad}(\ln \gamma_i) \tag{2}$$

where R is the ideal gas constant (J/mol/°K), F the Faraday constant (C/mol), T the temperature (°K), and z_i the valence of the ion.

The coefficient D_i^{μ} appearing in the equation is the diffusion coefficient in the liquid phase (i.e., at the microscopic scale). It represents the diffusion coefficient in an ideal solution (i.e., in a very dilute solution). The value of D_i^{μ} for chloride ions is 2.032×10^{-9} m^2/s [8].

The variable γ_i that appears in Eq. (2) is the chemical activity coefficient of the chemical species in solution. For concentrated solutions, it can be calculated using various semiempirical equations [4,6].

Finally, the variable ψ in Eq. (2) stands for the diffusion potential (volt) set up by the drifting ions. This local potential can be calculated on the basis of the Poisson equation, Eq. (3) [4,6]:

$$\nabla^2\psi - \frac{\rho}{\varepsilon} = 0 \tag{3}$$

Where ρ stands for the electrical charge density (C/m^3) and ε refers to the dielectric constant of the medium (F/m). The charge density is related to the concentration of the N ionic species through the relationship shown in Eq. (4):

$$\rho = F\sum_{i=1}^{N} z_i c_i \tag{4}$$

In electrochemistry, Eq. (2) is known as the extended Nernst-Planck equation. In order to keep the following mathematical derivations as simple as possible, the homogenization technique will only be applied to a simplified version of the Nernst-Planck equation in which chemical activity effects are neglected [see Eq. (5)]:

$$j_i = -D_i^{\mu}\mathrm{grad}(c_i) - \frac{D_i^{\mu} z_i F}{RT} c_i \mathrm{grad}(\psi) \tag{5}$$

The possible chemical reactions occurring in cement-based materials will also be neglected in this paper for simplicity.

3. Averaging over the representative elementary volume

Having established the transport equations at the microscopic scale, one faces various alternatives to describe the diffusion properties of the porous material at the macroscopic scale. Numerous authors have chosen to model the pore structure of cement systems on the basis of microstructural information such as that provided by mercury intrusion porosimetry [9]. Given the intrinsic complexity of the pore structure of most cement-based systems, the effective application of these data constitutes a formidable task [10]. In most cases, these models rely on “material’’ parameters (determined on the basis of simplified assumptions that may not physically represent the system well) to fully describe the intricate nature of the microporous solid.

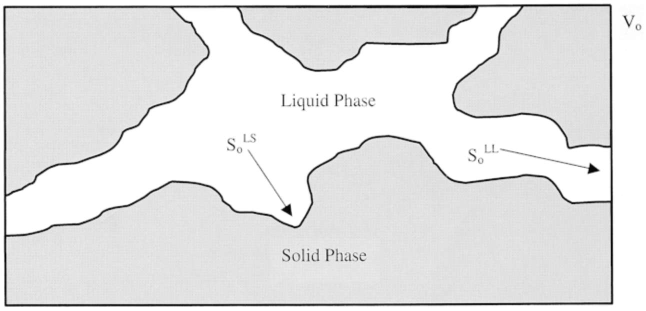

Fig. 1. The REV.

Another solution is to simply average the variables of interest over a representative elementary volume (REV). The main advantage of this approach (called the homogenization technique) is that it does not require any detailed knowledge of the material inner structure. Another significant advantage is that the new averaged variables appearing in the equations can easily be measured in practice.

The notion of the REV forms the basis of the homogenization technique. The REV should be large enough that its physical characteristics (porosity, paste fraction, etc.) are representative of the material. The REV can be characterized by various parameters (Fig. 1). V_o indicates the entire volume of material, V_o^L is the volume occupied by the liquid phase, S_o^{LS} represents the boundaries between the liquid and the solid phases, and S_o^{LL} is the liquid in contact with the external boundary of the REV [10].

The variable of interest for discussion of the mechanisms of ionic diffusion in porous media is the concentration. The volumetric phase average of c_i is given by Eq. (6):

$$\bar{c}_i \equiv \frac{1}{V_o}\int_{V_o^L} c_i \, dV \tag{6}$$

It is important to note that the new variable c_i is defined over the entire volume V_o.

Another useful definition is the volumetric intrinsic phase average, in which the averaging process is performed over a single specific phase, in our case the liquid phase, as shown in Eq. (7):

$$\bar{c}_i^L \equiv \frac{1}{V_o^L}\int_{V_o^L} c_i \, dV \tag{7}$$

where V_o^L is the volume of liquid phase in the REV. As with c_i, c_i^L is defined over the entire volume of the REV [11]. This value corresponds to the concentration that one might measure experimentally in a multiphase system.

One should also define a quantity called the volume fraction of the liquid phase, as seen in Eq. (8) [10]:

$$\theta \equiv \frac{V_o^L}{V_o} \tag{8}$$

It corresponds to the water content of the material. For a fully saturated material, it is equivalent to the porosity.

The two averages defined in Eq. (6) and Eq. (7) are related to each other through the volume fraction, as shown in Eq. (9):

$$\bar{c}_i = \theta \bar{c}_i^L \tag{9}$$

The fact that both averages c_i and c_i^L are defined over the REV has direct and important implications on the interpretation of the results provided by the application of the homogenization procedure. By averaging over the REV, the different phases found in various areas of the entire volume are replaced by overlapping continua evenly distributed over the entire domain [10,11,12].

Having established the above definition, the averaging procedures can be applied to the mass conservation law Eq. (1) and constitutive equation, Eq. (5). The average of the conservation law over all the REV (volumetric phase average) is given by Eq. (10):

$$\frac{1}{V_o}\int_{V_o^L}\left(\frac{\partial c_i}{\partial t} + \operatorname{div}(j_i)\right) dV = 0 \tag{10}$$

Utilizing the fact that the average of a sum equals the sum of the averages [10,12], Eq. (10) can be developed as Eq. (11):

$$\frac{1}{V_o}\int_{V_o^L}\frac{\partial c_i}{\partial t}\, dV + \frac{1}{V_o}\int_{V_o^L}\operatorname{div}(j_i)\, dV = 0 \tag{11}$$

Using the definition of the volumetric phase average [Eq. 6)], Eq. (11) can be modified as shown in Eq. (12):

$$\overline{\frac{\partial c_i}{\partial t}} + \overline{\operatorname{div}(j_i)} = 0 \tag{12}$$

combining Eq. (12) with Eq. (9), one finds [see Eq. (13)]:

$$\theta\overline{\frac{\partial c_i}{\partial t}}^L + \theta\overline{\operatorname{div}(j_i)}^L = 0 \tag{13}$$

It is necessary to calculate the average of a time derivative, the average of a divergence, and the average of a gradient to complete the homogenization procedure. They will be given without the appropriate demonstrations. More information on these mathematical operations can be found in the literature [10,12].

The average of a time derivative is given by Eq. (14):

$$\frac{\partial(\theta\bar{c}_i^L)}{\partial t} = \theta\overline{\frac{\partial c_i}{\partial t}}^L + \frac{1}{V_o^L}\int_{S_o^{LS}} c_i \, u \cdot n \, dS \tag{14}$$

where S^{LS} designates the surface of the solid/liquid interface (see Fig. 1), n is a vector normal to the surface S^{LS} and pointing outward, and u is the velocity of the surface. In the case of the diffusion of ions in concrete, $u = 0$. One can therefore write [see Eq. (15)]:

$$\frac{\partial(\theta\bar{c}_i^L)}{\partial t} = \theta\overline{\frac{\partial c_i}{\partial t}}^L \tag{15}$$

The average of the divergence is given by Eq. (16):

$$\theta\overline{\mathrm{div}(j_i)}^L = \mathrm{div}(\theta\bar{j}_i^L) + \frac{1}{V_o^L}\int_{S_o^{LS}} j_i \cdot n\, dS \tag{16}$$

The last term on the right-hand side of Eq. (16) describes the exchange between the liquid and the solid phase by a flux through the surface S_o^{LS}. In most practical cases, this term can be used to account for chemical reactions between the solid and the drifting ions.

However, for our present simplified case, this term can be neglected, leaving Eq. (17):

$$\theta\overline{\mathrm{div}(j_i)}^L = \mathrm{div}(\theta\bar{j}_i^L) \tag{17}$$

The average of a gradient is given by Eq. (18):

$$\overline{\mathrm{grad}(c_i)}^L = \left(\frac{1}{V_o^L}\int_{S_o^{LL}} n \otimes \overset{o}{x}\, dS\right)\mathrm{grad}(\bar{c}_i^L) + \frac{1}{V_o^L}\int_{S_o^{LS}} \mathrm{grad}(c_i)\cdot n\, dS \tag{18}$$

where S^{LL} designates the surface of the liquid phase in contact with the liquid phase of the adjacent REVs (see Fig. 1) and x^o is the position of a point on S_o^{LL} relative to the center of the REV. The term within the first parenthesis on the right-hand side of Eq. (18) corresponds to the tortuosity of the pore system, τ [10]. It is a second-rank tensor and gives information on the complexity of the shape of the porous network. It should be emphasized, however, that the evaluation of the tortuosity on the basis of this expression is difficult.

The last term in Eq. (18) accounts for the exchange by diffusion between the liquid and the solid phases. In the case of concrete, it can be neglected since the diffusion in the solid phase is insignificant. The exchange between the two phases, when it occurs, should be modeled using the last term in Eq. (16).

With all these considerations, the final expression for the average of a gradient is shown in Eq. (19):

$$\overline{\mathrm{grad}(c_i)}^L = \tau\,\mathrm{grad}(\bar{c}_i^L) \tag{19}$$

The average of a product is given by Eq. (20):

$$\overline{c_i\mathrm{grad}(\psi)}^L = \bar{c}_i^L\,\overline{\mathrm{grad}(\psi)}^L + \overline{\overset{o}{c}_i\ \overset{o}{\mathrm{grad}}\ (\psi)}^L \tag{20}$$

where the terms $\overset{o}{c}_i$ and $\overset{o}{\mathrm{grad}}(\psi)$ are the deviations of the given variable around the average value. They can be neglected [10], thus leaving [see Eq. (21)]:

$$\overline{c_i\mathrm{grad}(\psi)}^L = \bar{c}_i^L\,\overline{\mathrm{grad}(\psi)}^L \tag{21}$$

By substituting Eq. (15) and Eq. (17) in Eq. (13), the average of the mass conservation equation can be expressed as shown in Eq. (22):

$$\frac{\partial(\theta\bar{c}_i^L)}{\partial t} = \mathrm{div}(\theta\bar{j}_i^L) \tag{22}$$

As can be seen in the last equation, one should finally develop an expression for the average value of the ionic flux. Following Eq. (5), one can write Eq. (23):

$$\bar{j}_i^L = -D^\mu\overline{\mathrm{grad}(c_i)}^L - \frac{D_i^\mu z_i F}{RT}\overline{c_i\mathrm{grad}(\psi)}^L \tag{23}$$

Combining Eq. (23) with Eq. (19) and Eq. (21), the final expression of the flux is given by Eq. (24):

$$\bar{j}_i^L = -D_i^\mu\tau\mathrm{grad}(\bar{c}_i^L) - \frac{D_i^\mu z_i F\tau}{RT}\bar{c}_i^L\,\mathrm{grad}(\bar{\psi}^L) \tag{24}$$

A new diffusion coefficient is defined as seen in Eq. (25):

$$D_i = D_i^\mu\tau \tag{25}$$

It corresponds to the diffusion coefficient at the macroscopic scale. It is important to remember that this new parameter is nothing more than the ionic diffusion coefficient at microscopic scale (i.e., the liquid phase), modified by a purely geometrical factor accounting for the complexity of the porous system.

The variable ψ^L that appears in Eq. (24) represents the value of the electrical potential ψ in the liquid phase averaged over the REV.

Expressing Eq. (24) and Eq. (25) in the averaged form of the mass conservation law [Eq. (22)], the diffusion model based on an averaged concentration c_i^L becomes [see Eq. (26)]:

$$\frac{\partial(\theta\bar{c}_i^L)}{\partial t} = \mathrm{div}\left(-\theta D_i\mathrm{grad}(\bar{c}_i^L) - \theta\frac{D_i z_i F}{RT}\bar{c}_i^L\,\mathrm{grad}(\bar{\psi}^L)\right) \tag{26}$$

This equation can be used to model the diffusion of ions in a porous media where activity effects and chemical binding are neglected.

For the particular case of a fully saturated concrete with no variation in water content θ, Eq. (26) can be written as Eq. (27):

$$\frac{\partial(\bar{c}_i^L)}{\partial t} = \mathrm{div}\left(-D_i\mathrm{grad}(\bar{c}_i^L) - \frac{D_i z_i F}{RT}\bar{c}_i^L\,\mathrm{grad}(\bar{\psi}^L)\right) \tag{27}$$

This is Nernst-Planck equation at the macroscopic scale. It describes an ionic species by the average concentration in the liquid phase. The diffusion is controlled by D_i, which hides the effects of the complex geometry of the porous network of the concrete. This law is often use to model ionic diffusion in concrete, but without the homogenization technique, it is difficult to understand the meaning of each parameter in the equation.

It should be emphasized that the diffusion coefficient D_i (as defined in the last equations) is a property of the porous network and of the ionic species under consideration, while the tortuosity coefficient τ is a characteristic of the solid solely. From an engineering point of view, the determination of the tortuosity coefficient on the basis of experimental tests is quite important since it provides information on the ability of the solid to impede ion transport.

To complete the model, the averaging procedure is performed on the Poisson equation [see Eq. (3) and Eq. (4)]. It gives Eq. (28):

$$\mathrm{div}(\theta\tau\,\mathrm{grad}(\overline{\psi}^L)) + \theta\frac{F}{\varepsilon}\left(\sum_{i=1}^{N} z_i\overline{c}_i^L\right) = 0 \qquad (28)$$

It should also be noted that neither the tortuosity coefficient nor the diffusion coefficient should be influenced by parameters such as the type and the number of coexisting ions or the concentrations of the external solutions in contact with the solid. As previously discussed, the Nernst-Planck/Poisson set of equations already takes into account the interaction between the various ionic fluxes that may take place during the diffusion process. The system of equations can be easily modified to account for chemical activity effects or the chemical interactions of the ionic species with the solid phases.

4. Concluding remarks

Is has been demonstrated that the homogenization technique, based on the averaging of the conservation law and constitutive equation at microscopic scale, can describe the transport of ions at the material scale. The technique was applied to the case of a very simple constitutive equation (Nernst-Planck). More complex constitutive laws, for example the extended Nernst-Planck equation, could be used in the model and averaged over the REV through the same procedure.

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