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Modeling ion and fluid transport in unsaturated cement systems in isothermal conditions

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Abstract

A description of ionic transport in unsaturated porous materials due to gradients in the electro-chemical potential and the moisture content is developed by averaging the relevant microscopic transport equations over a representative volume element. The complete set of equations consists of time-dependent equations for both the concentration of ionic species within the pore solution and the moisture content within the pore space. The electrostatic interactions are assumed to occur instantaneously, and the resulting electrical potential satisfies Poisson's equation. Using the homogenization technique, moisture transport due to both the liquid and vapor phases is shown to obey Richards' equation, and a precise definition of the moisture content is found. The final transport equations contain transport coefficients that can be unambiguously related to experimental quantities. The approach has the advantage of making the distinction between microscopic and bulk quantities explicit.

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1. Introduction

Over the past decade, a great deal of effort has been specifically devoted to the investigation of ion transport mechanisms in unsaturated cement systems. The topic is important because, in many cases, concrete structures exposed to ionic solutions are also frequently subjected to wetting and drying cycles. The coupled transport of moisture and ions often tends to accelerate physical and chemical degradation mechanisms and reduce the service life of the material [1–3].

Reports recently published on the subject have largely contributed to clarify some fundamental aspects of ion transport mechanisms in unsaturated concrete. Many inves-

tigations have also emphasized the intricate nature of these phenomena. If most of the difficulties related to the description of transport processes in concrete are linked to the intrinsic complexity of the material, it appears that part of them also lies with the fact that authors have used many different approaches to study these processes. For instance, the definitions of the state variables used to describe the various transport processes tend to vary significantly from one study to another. This is most unfortunate because the lack of a unified approach often contributes to confuse the issue.

This paper is an attempt to clarify some fundamental aspects of the problem. The transport mechanisms are described using a well-established mathematical procedure, the homogenization technique. The technique has been recently used to investigate the diffusion of ions in saturated systems [4]. According to this approach, the transport equations are first written at the pore scale. They are then averaged over the scale of the material. The main advantage

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of the homogenization technique lies in the clear definition of the state variables.

The paper first addresses the process of moisture transport in an unsaturated porous material. For the completely coupled transport of ions in an unsaturated media, dynamical equations are required to express the moisture content as a function of time. This is achieved by averaging microscopical equations for both liquid and water vapor transport. The mathematical development yields the Richards' equation, and the moisture content and the transport coefficients are well defined.

The second part of the paper is devoted to the coupled transport of ions and moisture in the system. Here, the field quantity is the concentration of the ions within the pore solution. The homogenization technique is applied to a microscopic equation for both diffusive and convective transport. While diffusive equations already exist, reformulating the bulk equations using homogenization ensures that the transport coefficients are well defined (pore space versus microscopic quantities) and can therefore be unambiguously related to experimental quantities.

2. Water transport in unsaturated porous materials

The first objective is to develop an equation to characterize the mass transport of water in an unsaturated porous material. Richards [5] was among the first authors to study the mechanisms of water transport in unsaturated porous solids. In 1931, he proposed the following equation to describe the flow of water under capillary suction:

$$\frac{\partial \theta}{\partial t} - \text{div}(K \text{grad} \Gamma) = 0 \quad (1)$$

where θ is the water content, K is the permeability of the porous material, and Γ is the capillary potential.

This relationship, known as Richards' equation, was later modified to express the transport of mass solely as a function of the gradient in water content. This modification is based on the assumption that the capillary potential Γ is a differentiable function of the moisture content θ :

$$\Gamma = f(\theta) \quad (2)$$

This allows to write:

$$\text{grad} \Gamma = \frac{d\Gamma}{d\theta} \text{grad} \theta \quad (3)$$

Substituting Eq. (3) into Eq. (1), one finds:

$$\frac{\partial \theta}{\partial t} - \text{div}(D_\theta \text{grad} \theta) \quad (4)$$

where $D_\theta = K(d\Gamma/d\theta)$ is the nonlinear water diffusivity coefficient. Eq. (4) is widely used to model the evolution of water content in a porous material kept in isothermal conditions. Eq. (4) is also known as Richards' equation.

While Richards' equation is commonly accepted among scientists, its use over the past decades has contributed to some confusion on how to describe moisture transport mechanisms in unsaturated porous materials. Richards originally wrote the equation with the water content expressed in cubic centimeters of water per gram of dry material. Over the years, some authors have preferred to define water content in kilograms of *moisture* per kilogram of dry material [6] or in kilograms of water per cubic meter of material [7,8]. However, most authors have traditionally chosen to express the variable in cubic meter of water per cubic meter of material [9–11]. To add to the confusion, many authors tend to define the *moisture content* as the sum of liquid water and vapor, while some others only consider the liquid phase.

2.1. General considerations

In an attempt to clarify these concepts, Richards' equation will be derived using the homogenization technique. To simplify the problem, the derivation is based on the assumptions that the isotropic porous material is an infinitely rigid solid (no significant deformations) kept under isothermal conditions (i.e., the transport of water is solely due to capillary suction). Other assumptions will arise during the development of the model.

The mathematical rules of the averaging technique can be found in textbooks [12,13]. Only the basic definitions will be exposed in the following paragraphs. More information on the technique can also be found in Ref. [4]. The technique is outlined here because it is at the core of development of all the transport equations.

As previously mentioned, the homogenization technique starts with a conservation and a transport equation at the microscopic level (i.e., at the scale of the pore). These equations are then integrated over a Representative Elementary Volume (REV), such as the one depicted in Fig. 1. The size of the volume depends on the intrinsic properties of the material. For instance, for concrete and mortar mixtures, the size of the REV depends on the maximum diameter of the aggregate particles. For the hydrated cement paste, the REV is typically a few cubic centimeters.

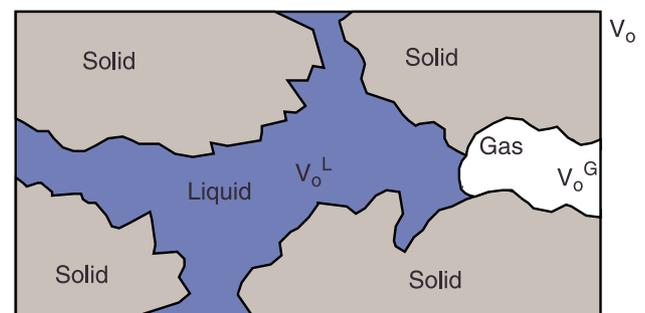


Fig. 1. The representative elementary volume (REV).

The total volume of the REV is given by V_o . The volume occupied by the liquid phase is designated by V_o^L . The volumetric fraction of liquid θ_L is the ratio of the liquid volume to the total volume:

$$\theta_L = \frac{V_o^L}{V_o} \quad (5)$$

The gaseous phase occupies a volume V_o^G . It is a mixture of air and water vapor. It is assumed that both air and the water vapor fill the whole gaseous phase volume. As for the liquid phase, the volumetric fraction of gas θ_G is the ratio of the gas volume to the total volume:

$$\theta_G = \frac{V_o^G}{V_o} \quad (6)$$

In the remainder of the text, the superscripts L and G will designate the liquid and gaseous phases, respectively. Furthermore, the superscript V will represent the water vapor phase within the total gaseous phase.

Let a_α denote the amount per unit volume of some extensive quantity A in the phase α , either solid, liquid, or gas. Concentration or mass density can serve as examples for a_α . Two averages can be defined. The *volumetric phase average* is given by:

$$\bar{a}_\alpha = \frac{1}{V_o} \int_{V_o^\alpha} a_\alpha dV \quad (7)$$

The *volumetric intrinsic phase average* is defined as:

$$\bar{a}_\alpha^\alpha = \frac{1}{V_o^\alpha} \int_{V_o^\alpha} a_\alpha dV \quad (8)$$

The two values are related by the following relationship:

$$\bar{a}_\alpha = \theta_\alpha \bar{a}_\alpha^\alpha \quad (9)$$

2.2. Transport of liquid water

The continuity equation for liquid water is given by [14,15]:

$$\frac{\partial \rho_L}{\partial t} + \text{div}(\rho_L \mathbf{v}_L) = 0 \quad (10)$$

where ρ_L is the mass of liquid water per unit volume of liquid phase and \mathbf{v}_L is the velocity of water. The bulk equation is obtained by averaging Eq. (10) over the REV:

$$\frac{1}{V_o} \int_{V_o^L} \left(\frac{\partial \rho_L}{\partial t} + \text{div}(\rho_L \mathbf{v}_L) \right) dV = 0 \quad (11)$$

This integral can be divided in two parts:

$$\frac{1}{V_o} \int_{V_o^L} \frac{\partial \rho_L}{\partial t} dV + \frac{1}{V_o} \int_{V_o^L} \text{div}(\rho_L \mathbf{v}_L) dV = 0 \quad (12)$$

Using the definition of the volumetric phase average (Eq. (7)), one can write:

$$\frac{\partial \bar{\rho}_L}{\partial t} + \overline{\text{div}(\rho_L \mathbf{v}_L)} = 0 \quad (13)$$

The average of the time derivative gives [12,13]:

$$\begin{aligned} \frac{\partial(\theta_L \bar{\rho}_L^L)}{\partial t} &= \frac{\partial \bar{\rho}_L}{\partial t} + \frac{1}{V_o} \int_{S_o^{LG}} \rho_L \mathbf{u} \cdot \mathbf{n}_{LG} dS \\ &+ \frac{1}{V_o} \int_{S_o^{LS}} \rho_L \mathbf{u} \cdot \mathbf{n}_{LS} dS \end{aligned} \quad (14)$$

where S_o^{LG} is the surface of the liquid/gas interface, S_o^{LS} is the surface of the liquid/solid interface, \mathbf{u} is the velocity of the interface, \mathbf{n}_{LG} is a unit vector pointing outward the liquid phase at the liquid/gas interface, and \mathbf{n}_{LS} is a unit vector pointing outward the liquid phase at the liquid/solid interface. Because it is assumed that the deformations of the solid matrix could be neglected, the last integral on the right-hand side of Eq. (14) can be dropped, which leaves:

$$\frac{\partial(\theta_L \bar{\rho}_L^L)}{\partial t} = \frac{\partial \bar{\rho}_L}{\partial t} + \frac{1}{V_o} \int_{S_o^{LG}} \rho_L \mathbf{u} \cdot \mathbf{n}_{LG} dS \quad (15)$$

The average of the divergence in Eq. (13) is given by [12,13]:

$$\begin{aligned} \overline{\text{div}(\rho_L \mathbf{v}_L)} &= \text{div}(\theta_L \overline{(\rho_L \mathbf{v}_L^L)}) + \frac{1}{V_o} \\ &\times \int_{S_o^{LG}} \rho_L \mathbf{v}_L \cdot \mathbf{n}_{LG} dS + \frac{1}{V_o} \\ &\times \int_{S_o^{LS}} \rho_L \mathbf{v}_L \cdot \mathbf{n}_{LS} dS \end{aligned} \quad (16)$$

At the solid/liquid interface, it is assumed that the liquid velocity is zero (the so-called no-slip condition of fluid mechanics [16]). Hence, the last integral on the right-hand side of Eq. (16) can be neglected, which leaves:

$$\begin{aligned} \overline{\text{div}(\rho_L \mathbf{v}_L)} &= \text{div}(\theta_L \overline{(\rho_L \mathbf{v}_L^L)}) + \frac{1}{V_o} \\ &\times \int_{S_o^{LG}} \rho_L \mathbf{v}_L \cdot \mathbf{n}_{LG} dS \end{aligned} \quad (17)$$

Substituting Eqs. (15) and (17) in Eq. (13), one finds:

$$\begin{aligned} \frac{\partial(\theta_L \bar{\rho}_L^L)}{\partial t} + \text{div}(\theta_L \overline{(\rho_L \mathbf{v}_L^L)}) \\ + \frac{1}{V_o} \int_{S_o^{LG}} \rho_L (\mathbf{v}_L - \mathbf{u}) \cdot \mathbf{n}_{LG} dS = 0 \end{aligned} \quad (18)$$

According to Whitaker [15], the integral in Eq. (18) corresponds to the rate of vaporization per unit volume of the liquid phase at the liquid/gas interface and is denoted by \bar{m} . In addition, the average value $\bar{\rho}_L^L$ corresponds to the density of the liquid ρ_L , which can be assumed constant. Eq. (18) can thus be simplified:

$$\rho_L \frac{\partial \theta_L}{\partial t} + \rho_L \operatorname{div}(\theta_L \bar{\mathbf{v}}_L^L) + \bar{m} = 0 \quad (19)$$

The next step consists of determining the average value of the liquid velocity. The starting point is the Darcy equation [17]:

$$\bar{\mathbf{v}}_L = -\frac{K}{\mu}(\operatorname{grad}P + \rho_L \mathbf{g}) \quad (20)$$

The quantity $\bar{\mathbf{v}}_L$ is the bulk velocity of the liquid, K is the permeability of the material, μ is the viscosity of the fluid, P is the pressure on the liquid, and \mathbf{g} is the gravitational acceleration. Darcy originally derived this equation to describe the transport of water through the material at the macroscopic scale. Whitaker [15] showed that in materials having very small pores, the capillary forces are dominant:

$$\bar{\mathbf{v}}_L = -\frac{k}{\mu} \theta_L \operatorname{grad} \bar{p}_c \quad (21)$$

The quantity p_c is the capillary pressure and k is the permeability of the liquid-filled pore space.

Eq. (21) is based on the assumptions that gravity effects are negligible and that the pressure is uniform throughout the liquid and gaseous phases. It should also be emphasized that the validity of the equation also rests on the hypothesis that the liquid phase is *continuous*. The latter assumption will be further discussed in the last section of this report.

The bulk velocity of the liquid $\bar{\mathbf{v}}_L$ can be related to its intrinsic average counterpart through:

$$\bar{\mathbf{v}}_L = \theta_L \bar{\mathbf{v}}_L^L \quad (22)$$

Substituting Eqs. (21) and (22) into Eq. (19) gives:

$$\rho_L \frac{\partial \theta_L}{\partial t} - \rho_L \operatorname{div} \left(\frac{K}{\mu} \theta_L \operatorname{grad} \bar{p}_c \right) + \bar{m} = 0 \quad (23)$$

Since $\bar{p}_c = f(\theta_L)$ [15], the chain rule allows to write:

$$\operatorname{grad} \bar{p}_c = \left(\frac{d\bar{p}_c}{d\theta_L} \right) \operatorname{grad} \theta_L \quad (24)$$

The substitution of Eq. (24) in Eq. (23) gives:

$$\rho_L \frac{\partial \theta_L}{\partial t} - \rho_L \operatorname{div} \left(\frac{K}{\mu} \theta_L \frac{d\bar{p}_c}{d\theta_L} \operatorname{grad} \theta_L \right) + \bar{m} = 0 \quad (25)$$

Let

$$D_L = \frac{K}{\mu} \theta_L \frac{d\bar{p}_c}{d\theta_L} \quad (26)$$

Eq. (25) is now expressed as a function of a single field quantity θ_L to give a complete description of liquid water transport:

$$\rho_L \frac{\partial \theta_L}{\partial t} - \rho_L \operatorname{div}(D_L \operatorname{grad} \theta_L) + \bar{m} = 0 \quad (27)$$

Since Eq. (27) is expressed in the form of a diffusion equation, D_L can be assimilated to a *water diffusion coefficient*. However, it should be emphasized that the movement of liquid water considered in this section arises by capillary suction. It is not, per se, a *diffusive phenomenon*.

With the definition of D_L given in Eq. (26), combined with Eq. (24), the velocity of the liquid phase (Eq. (21)) can now be written as:

$$\bar{\mathbf{v}}_L = -D_L \operatorname{grad} \theta_L \quad (28)$$

2.3. Transport of water vapor

The treatment of the gas transport phenomenon is more complicated because two phases have to be considered: air and water vapor. However, the problem can be simplified by considering the following assumptions. As mentioned in the previous section, the development of Eq. (21) rests on the hypothesis that pressure is uniform over the gaseous phase. This implies that there is no bulk movement of air in the gaseous phase. Consequently, there will be no convective transport of water vapor within the material pore structure. Still, there can be movement of molecules in the gaseous phase as a result of their thermal agitation. The other assumption is that gravity does not have any significant effect on the behavior of the water vapor.

The continuity equation for water vapor component of a gaseous phase is the following [15]:

$$\frac{\partial \rho_V}{\partial t} + \operatorname{div}(\rho_V \mathbf{v}_V) = 0 \quad (29)$$

The quantity ρ_V is the mass of water vapor per unit volume of gaseous phase, and \mathbf{v}_V is the velocity of water vapor. The water vapor will be in movement as a result of its thermal agitation. It is therefore a *diffusive* process. According to Daian [10], the water vapor flux is given as:

$$\rho_V \mathbf{v}_V = -D \operatorname{grad} \rho_V \quad (30)$$

where D is the self-diffusion coefficient of water vapor in the gaseous phase. By combining Eqs. (29) and (30), one gets:

$$\frac{\partial \rho_V}{\partial t} - \operatorname{div}(D \operatorname{grad} \rho_V) = 0 \quad (31)$$

The bulk equation is calculated from the integration of Eq. (31) over the REV:

$$\frac{1}{V_o} \int_{V^G} \left(\frac{\partial \rho_V}{\partial t} - \operatorname{div}(D \operatorname{grad} \rho_V) \right) dV = 0 \quad (32)$$

This integral can be divided in two parts, which yields:

$$\frac{1}{V_o} \int_{V^G} \frac{\partial \rho_V}{\partial t} dV - \frac{1}{V_o} \int_{V^G} \text{div}(D \text{grad} \rho_V) dV = 0 \quad (33)$$

According to the definition of the volumetric phase average (Eq. (7)), Eq. (33) can be written as:

$$\overline{\frac{\partial \rho_V}{\partial t}} - \overline{\text{div}(D \text{grad} \rho_V)} = 0 \quad (34)$$

The average of the time derivative is given by:

$$\begin{aligned} \frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} &= \frac{\partial \overline{\rho_V}}{\partial t} + \frac{1}{V_o} \int_{S_o^{GL}} \rho_V \mathbf{u} \cdot \mathbf{n}_{GL} dS \\ &+ \frac{1}{V_o} \int_{S_o^{GS}} \rho_V \mathbf{u} \cdot \mathbf{n}_{GS} dS \end{aligned} \quad (35)$$

where S_o^{GL} is the surface of the liquid/gas interface, S_o^{GS} is the surface of the gas/solid interface, \mathbf{u} is the velocity of the interface, \mathbf{n}_{GL} is a unit vector pointing outward the gaseous phase at the liquid/gas interface, and \mathbf{n}_{GS} is a unit vector pointing outward the gaseous phase at the gas/solid interface. Because it is assumed that the deformations of the solid matrix are negligible, the last integral on the right-hand side of Eq. (35) can be neglected, which leaves:

$$\frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} = \frac{\partial \overline{\rho_V}}{\partial t} + \frac{1}{V_o} \int_{S_o^{GL}} \rho_V \mathbf{u} \cdot \mathbf{n}_{GL} dS \quad (36)$$

The average of the divergence gives:

$$\begin{aligned} \overline{\text{div}(D \text{grad} \rho_V)} &= \text{div}(\theta_G \overline{D \text{grad} \rho_V^G}) \\ &+ \frac{1}{V_o} \int_{S_o^{GS}} D \text{grad} \rho_V \cdot \mathbf{n}_{GS} dS \\ &+ \frac{1}{V_o} \int_{S_o^{GL}} D \text{grad} \rho_V \cdot \mathbf{n}_{GL} dS \end{aligned} \quad (37)$$

The first integral on the right-hand side of Eq. (37) is neglected because there is no exchange of water vapor between the solid and the gaseous phases. Accordingly, Eq. (37) can be simplified as:

$$\begin{aligned} \overline{\text{div}(D \text{grad} \rho_V)} &= \text{div}(\theta_G \overline{D \text{grad} \rho_V^G}) \\ &+ \frac{1}{V_o} \int_{S_o^{GL}} D \text{grad} \rho_V \cdot \mathbf{n}_{GL} dS \end{aligned} \quad (38)$$

Furthermore, by assuming that the coefficient D is constant, Eq. (38) can be written as:

$$\begin{aligned} \overline{\text{div}(D \text{grad} \rho_V)} &= \text{div}(\theta_G \overline{D \text{grad} \rho_V^G}) \\ &+ \frac{1}{V_o} \int_{S_o^{GL}} D \text{grad} \rho_V \cdot \mathbf{n}_{GL} dS \end{aligned} \quad (39)$$

The average of the gradient is given by [12,13]:

$$\begin{aligned} \overline{\text{grad} \rho_V^G} &= \tau_G \text{grad} \overline{\rho_V^G} + \frac{1}{V_o} \int_{S_o^{GS}} \hat{\mathbf{x}}(\text{grad} \rho_V \cdot \mathbf{n}_{GS}) dS \\ &+ \frac{1}{V_o} \int_{S_o^{GL}} \hat{\mathbf{x}}(\text{grad} \rho_V \cdot \mathbf{n}_{GL}) dS \end{aligned} \quad (40)$$

The quantity τ is referred to by Bachmat and Bear [12] as the tortuosity of the material. Conceptually, it is the ratio of the macroscopic system length to the shortest path length through the pore (liquid or gas) space. As such, it is a quantity that strictly equal to or less than one. The parameter $\hat{\mathbf{x}}$ is defined as $\hat{\mathbf{x}} = \mathbf{x} - \mathbf{x}_o$, where \mathbf{x} is a position vector within the REV and \mathbf{x}_o is the position vector of the center of the REV. The first integral on the right-hand side of Eq. (40) involves the solid/gas interface. Except for the very low water content conditions, there will be no direct contact between these two phases because water will be adsorbed on the surface of the solid. Accordingly, the integral can be neglected. It is assumed that the term $(\text{grad} \rho_V \cdot \mathbf{n}_{GL})$ in the second integral on the right-hand side of Eq. (40) varies very slightly over the surface S_o^{GL} . Under this assumption, it leaves an integral of a position vector times a scalar over a closed surface, which gives zero. Eq. (40) is thus simplified as:

$$\overline{\text{grad} \rho_V^G} = \tau_G \text{grad} \overline{\rho_V^G} \quad (41)$$

Replacing Eqs. (36), (39), and (41) into Eq. (34) gives:

$$\begin{aligned} \frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} - \text{div}(\theta_G D \tau_G \text{grad} \overline{\rho_V^G}) \\ + \frac{1}{V_o} \int_{S_o^{GL}} (D \text{grad} \rho_V - \rho_V \mathbf{u}) \cdot \mathbf{n}_{GL} dS = 0 \end{aligned} \quad (42)$$

Substituting Eq. (30) in Eq. (42), one finds:

$$\begin{aligned} \frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} - \text{div}(\theta_G D \tau_G \text{grad} \overline{\rho_V^G}) \\ - \frac{1}{V_o} \int_{S_o^{GL}} \rho_V (\mathbf{v}_V - \mathbf{u}) \cdot \mathbf{n}_{GL} dS = 0 \end{aligned} \quad (43)$$

Withaker [15] showed that the integral in Eq. (43) has the same value as the one in Eq. (18). It represents the rate of condensation per unit volume of the water vapor phase at the liquid/gas interface. Therefore, Eq. (43) can be written as:

$$\frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} - \text{div}(\theta_G D \tau_G \text{grad} \overline{\rho_V^G}) - \overline{\dot{m}} = 0 \quad (44)$$

It is possible to express the gradient in Eq. (44) as a function of θ_L since $\rho_V = f(\theta_L)$ [10]. Applying the chain rule, it gives:

$$\frac{\partial(\theta_G \overline{\rho_V^G})}{\partial t} - \text{div} \left(\theta_G D \tau_G \frac{d \overline{\rho_V^G}}{d \theta_L} \text{grad} \theta_L \right) - \overline{\dot{m}} = 0 \quad (45)$$

The quantities preceding the gradient within the parenthesis can be lumped together to form a single vapor diffusion coefficient:

$$D_V = \theta_G D_{\tau_G} \quad (46)$$

Eq. (45) can be written succinctly:

$$\frac{\partial(\theta_G \bar{\rho}_V^G)}{\partial t} - \text{div} \left(D_V \frac{d\bar{\rho}_V^G}{d\theta_L} \text{grad}\theta_L \right) - \bar{m} = 0 \quad (47)$$

2.4. Total moisture transport

In the previous sections, the transport equations for the liquid and the vapor phases were considered separately (Eqs. (27) and (47)). To get a complete description of the transport, both equations should be added together:

$$\frac{\partial}{\partial t} (\rho_L \theta_L + \theta_G \bar{\rho}_V^G) - \text{div} \left(\left(\rho_L D_L + \frac{d\bar{\rho}_V^G}{d\theta_L} D_V \right) \text{grad}\theta_L \right) = 0 \quad (48)$$

As the density of water vapor has a much lower value than the one of liquid water ($\bar{\rho}_V^G \ll \rho_L$) and $\theta_G \approx \theta_L$, Eq. (48) can be simplified as:

$$\rho_L \frac{\partial \theta_L}{\partial t} - \text{div} \left(\left(\rho_L D_L + \frac{d\bar{\rho}_V^G}{d\theta_L} D_V \right) \text{grad}\theta_L \right) = 0 \quad (49)$$

Let

$$D_\theta = \frac{\rho_L D_L + \frac{d\bar{\rho}_V^G}{d\theta_L} D_V}{\rho_L} \quad (50)$$

Substituting Eq. (50) into (49) gives:

$$\frac{\partial \theta_L}{\partial t} - \text{div}(D_\theta \text{grad}\theta_L) = 0 \quad (51)$$

This is Richards' equation. As can be seen, the equation fully describes the movement of both vapor and liquid water on the basis of a single variable θ_L . The influence of both phases is taken into account through the function D_θ , which contains a term associated to the vapor transport and a second one related to the transport of the liquid phase. The demonstration also indicates that the variable θ of the original Eq. (4) stands for the volumetric liquid water content, which is expressed in cubic meter of water per cubic meter of material.

2.5. Determination of the moisture transport properties of hydrated cement systems

The description of moisture transport mechanisms on the basis of Eq. (51) requires the determination of the function D_θ . An interesting discussion of the variation of this function with the water content of the material has recently

been published by Martys [19]. The author clearly emphasizes the nonlinear character of this function.

Measurements made on a sand column [20] show that when the humidity in the medium is higher than 4% (by weight), the contribution of the vapor phase to the overall moisture transfer is negligible. In that case, one can assume that $D_\theta = D_L$.

Over the years, numerous experimental techniques have been used to determine the moisture transport properties of hydrated cement systems. A thorough discussion of this subject is beyond the scope of this paper. Comprehensive critical reviews of this problem can be found in references [21,22].

3. Ionic transport in unsaturated porous materials

Several mathematical models have been developed to predict the movement of ions in cement-based materials. Most of these approaches are single-ion models, considering only chloride and its detrimental effect on the durability of the material. Most of the time, such models consider the transport of ions under the effect of diffusion and advection (fluid flow). Also considered is the effect of the chemical reactions involving the considered species, although in a very simple way. For example, Saetta et al. [23], Nagesh and Bhattacharjee [24], and Gospodinov et al. [25] published such models.

However, these models oversimplify some basic physical phenomena. For instance, the electrical coupling between the ions [18] and its effect on their movements is often overlooked. This is particularly true for cement-based materials because they contain concentrated porous solution. The electrical coupling between the ions for concentrated solutions was recently put in evidence in two papers by Snyder [26,27] that report on diffusion experiments through nonreactive ceramic frits. Multiionic models taking into account electrical coupling were recently published by Masi et al. [28] and Truc et al. [29].

Unfortunately, as it was the case with Richards' equation, there is a lack of agreement with regard to the definition and the use of some parameters in these models. For example, the diffusion coefficient is sometimes called the intrinsic diffusion coefficient, the apparent diffusion coefficient, or the effective diffusion coefficient. Once again, the averaging procedure is used to generate an ionic transport model. The method will clarify some of the basic concepts behind the modeling of ionic transport. Such a work was previously published [4] but was applied only to nonreactive saturated materials. The model presented in the following sections is more general.

3.1. Transport of ions in the liquid phase

The transport model is based on the observation that the transport of ions only occurs in the liquid phase. Hence, no

equation has to be developed for the solid or gaseous phase. The conservation equation for an ionic species i in the liquid phase at pore scale is given by the following microscopic equation [13]:

$$\frac{\partial c_i}{\partial t} + \text{div}(\mathbf{j}_i) + r_i = 0 \quad (52)$$

The quantity c_i is the concentration, \mathbf{j}_i is the ionic flux, and r_i is a source/sink term accounting for the homogeneous chemical reactions [39] between ions in solution. The bulk equation is obtained from averaging this equation over the REV, following the procedure that lead to Eqs. (13) and (34):

$$\overline{\frac{\partial c_i}{\partial t}} + \overline{\text{div}(\mathbf{j}_i)} + \overline{r_i} = 0 \quad (53)$$

The average of the time derivative leads to:

$$\begin{aligned} \frac{\partial(\theta_L \overline{c_i^L})}{\partial t} &= \frac{\partial \overline{c_i}}{\partial t} + \frac{1}{V_o} \int_{S_o^{LS}} c_i \mathbf{u} \cdot \mathbf{n}_{LS} \, dS \\ &+ \frac{1}{V_o} \int_{S_o^{LG}} c_i \mathbf{u} \cdot \mathbf{n}_{LG} \, dS \end{aligned} \quad (54)$$

The first integral on the right-hand side of Eq. (54) contains a term that accounts for the velocity of the solid/liquid interface. While this interface may possibly move as a result of some dissolution/precipitation chemical reactions, it will do so very slowly. It can thus be neglected. The other integral involves the movement of the liquid/gas interface. It is similar to the first integral in Eq. (14). While it was used in the mathematical development of the moisture transport, it is assumed that it has only a small effect on the ionic transport and can thus be neglected, simplifying Eq. (54) to:

$$\frac{\partial(\theta_L \overline{c_i^L})}{\partial t} = \frac{\partial \overline{c_i}}{\partial t} \quad (55)$$

The average of the divergence is given by:

$$\begin{aligned} \overline{\text{div}(\mathbf{j}_i)} &= \text{div}(\theta_L \overline{\mathbf{j}_i^L}) + \frac{1}{V_o} \int_{S_o^{LS}} \mathbf{j}_i \cdot \mathbf{n}_{LS} \, dS \\ &+ \frac{1}{V_o} \int_{S_o^{LG}} \mathbf{j}_i \cdot \mathbf{n}_{LG} \, dS \end{aligned} \quad (56)$$

The last integral on the right-hand side of Eq. (56) accounts for the ionic flux crossing the liquid/gaseous interface. The value of this flux is zero because ions do not go into the gaseous phase. The other integral, related to the flux of ions across the solid/liquid interface, will be used to model the various chemical reactions involving those phases. Accordingly, Eq. (56) can be reduced to:

$$\overline{\text{div}(\mathbf{j}_i)} = \text{div}(\theta_L \overline{\mathbf{j}_i^L}) + \frac{1}{V_o} \int_{S_o^{LS}} \mathbf{j}_i \cdot \mathbf{n}_{LS} \, dS \quad (57)$$

Substituting Eqs. (55) and (57) in Eq. (53) and averaging the term $\overline{r_i}$ by $\theta_L \overline{r_i^L}$ (see Eq. (9)), one finds:

$$\frac{\partial(\theta_L \overline{c_i^L})}{\partial t} + \text{div}(\theta_L \overline{\mathbf{j}_i^L}) + \theta_L \overline{r_i^L} + \frac{1}{V_o} \int_{S_o^{LS}} \mathbf{j}_i \cdot \mathbf{n}_{LS} \, dS = 0 \quad (58)$$

The next step consists of writing the proper flux expression at the microscopic level (ions in bulk electrolyte) and averaging it over the REV. Due to the charged nature of ions, this expression has to consider the electrical coupling between ionic particles. Furthermore, because the pore solution of cement-based materials is highly concentrated, it deviates from the ideal behavior of a dilute solution, requiring consideration of the chemical activity. Finally, the movement of the fluid itself will have an impact on the movement of ions. All these physical phenomena can be taken into account through the extended Nernst-Planck model to which is added an advection term [18]:

$$\mathbf{j}_i = -D_i^{\mu} \text{grad} c_i - \frac{D_i^{\mu} z_i F}{RT} c_i \text{grad} \psi - D_i^{\mu} c_i \text{grad}(\ln \gamma_i) + c_i \mathbf{v}_L \quad (59)$$

The parameter D_i^{μ} is the self-diffusion coefficient [30] of species i in diluted, free water conditions, γ_i is the chemical activity coefficient, ψ is the electrical potential, z_i is the valence number of the ion, F is the Faraday constant, R is the ideal gas constant, and T is the absolute temperature. The terms on the right-hand side of Eq. (59) are associated with diffusion, electrical coupling between the ions, chemical activity effects, and water transport, respectively.

The integration of the flux over the REV, similar to the procedure followed in Eqs. (9) and (11)–(13), leads to:

$$\begin{aligned} \theta_L \overline{\mathbf{j}_i^L} &= -D_i^{\mu} \theta_L \overline{\text{grad} c_i^L} - \frac{D_i^{\mu} z_i F}{RT} \theta_L \overline{c_i \text{grad} \psi^L} \\ &- D_i^{\mu} \overline{\theta_L c_i \text{grad}(\ln \gamma_i)^L} + \theta_L \overline{c_i \mathbf{v}_L^L} \end{aligned} \quad (60)$$

The next steps consist in averaging the various gradients and variables in Eq. (60).

The average of the concentration gradient is given by [12,13]:

$$\begin{aligned} \overline{\text{grad} c_i^L} &= \tau_L \text{grad} \overline{c_i^L} + \frac{1}{V_o} \int_{S_o^{LS}} \hat{\mathbf{x}} (\text{grad} c_i \cdot \mathbf{n}_{LS}) \, dS \\ &+ \frac{1}{V_o} \int_{S_o^{LG}} \hat{\mathbf{x}} (\text{grad} c_i \cdot \mathbf{n}_{LG}) \, dS \end{aligned} \quad (61)$$

The quantity τ_L is the tortuosity of the aqueous phase. It is a purely geometrical factor, accounting for the complexity of the paths the ions must travel through in liquid space. It is a function of the water content θ_L because it is related to the volume of liquid in the pore space, and its value is less than one [12]. The parameter $\hat{\mathbf{x}}$ was first encountered in Eq. (40).

To evaluate the surface integrals in Eq. (61), one has to refer to the double-layer theory [31]. Fig. 2 shows the cross-section of a pore and the schematic shape of the concentration profile along its radius. The solid bears an electrical surface charge σ_{solid} . It is neutralized by charges of the opposite sign in two different zones, the Stern and the diffuse layers, bearing, respectively, σ_{stern} and σ_{diff} charge per unit area. The electrical balance respects the following expression:

$$\sigma_{\text{solid}} = \sigma_{\text{stern}} + \sigma_{\text{diff}} \quad (62)$$

The external limit of the Stern layer, called the outer Helmholtz plane or the shear plane, separates the solid from the aqueous phase, in which ionic diffusion occur. The aqueous phase is divided in the diffuse layer and the free water zone, where ions do not feel the effect of the solid/liquid interface. A recent study by Revil [32] showed that ionic transport may occur in the Stern layer. But it was also mentioned in the paper that this phenomenon is negligible with respect to transport in the bulk pore when the pore solution is highly concentrated, as it is the case in cement-based materials. Consequently, only the ionic transport in the aqueous phase is considered in this paper. Finally, the description of the cross-section of the pore is complete by considering a gaseous phase at the center of the pore, when the latter is not saturated [33].

It is assumed that the concentration profiles at the liquid/gas interface is flat (see Fig. 2). Consequently, the second integral in Eq. (61) is negligible because there is no concentration gradient along the radius at the liquid/gas interface. The situation is different for the first integral because of the concentration gradient along the radius at the solid/liquid interface caused by the electric charge at the surface of the solid. Simple double-layer calculations made with the Gouy–Chapman model [31] are shown on Fig. 3. They emphasize that increasing the ionic strength of a

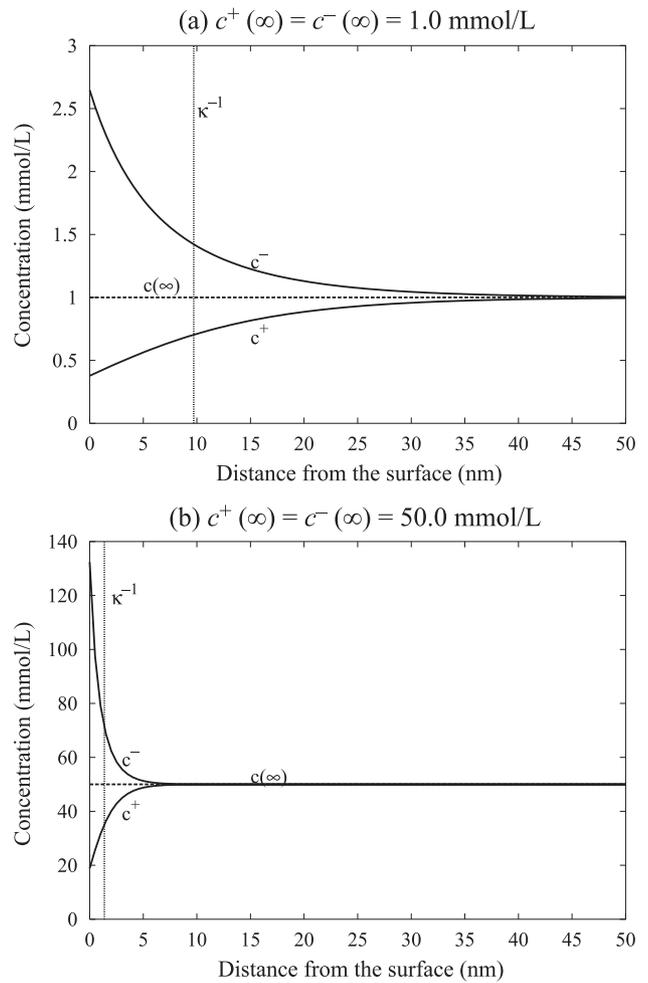


Fig. 3. Concentration profiles of a 1–1 electrolyte near a charged surface calculated with the Gouy–Chapman double-layer model. The calculations were made with a surface potential of 25 mV. The Debye length κ^{-1} is indicated.

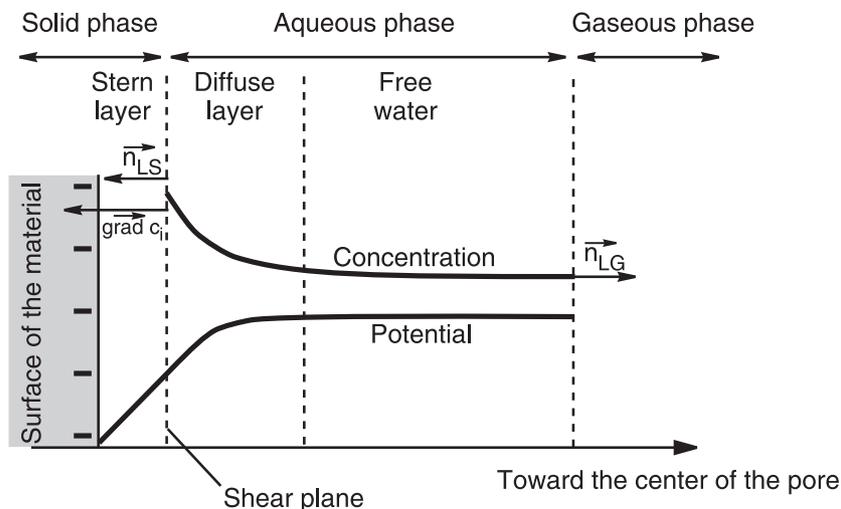


Fig. 2. Concentration and potential profile across a pore near the solid/liquid interface according to the double-layer theory.

solution in the vicinity of a charged surface decreases dramatically the thickness of the double layer. Since cementitious materials bear a highly charged solution, the double layer extends over a very small region. Outside this region, the concentration profile is unaffected by the surface charge. Following this, the term $\int \dot{\mathbf{x}}(\text{grad}c_i \cdot \mathbf{n}_{LS})dS$ in Eq. (61) is neglected, leaving:

$$\overline{\text{grad}c_i}^L = \tau_L \text{grad}c_i^L \quad (63)$$

Then one needs to average the term in Eq. (60) concerned with the electrical coupling between the ions. According to the procedure for averaging a product [12,13], one can write:

$$\overline{c_i \text{grad}\psi}^L = \overline{c_i}^L \overline{\text{grad}\psi}^L + \overline{c_i^{\circ} \text{grad}\psi}^L \quad (64)$$

where the quantities topped by $^{\circ}$, called deviations, are defined as:

$$c_i^{\circ} = c_i - \overline{c_i}^L \quad (65)$$

It is assumed that the deviations lead to small terms, which allows to neglect the deviation product in Eq. (64):

$$\overline{c_i \text{grad}\psi}^L = \overline{c_i}^L \overline{\text{grad}\psi}^L \quad (66)$$

Following the same procedure as the one used for the concentration gradient, the average of the potential gradient gives:

$$\begin{aligned} \overline{\text{grad}\psi}^L &= \tau_L \text{grad}\overline{\psi}^L + \frac{1}{V_o} \int_{S_o^{LS}} \dot{\mathbf{x}}(\text{grad}\Phi \cdot \mathbf{n}_{LS})dS \\ &+ \frac{1}{V_o} \int_{S_o^{LG}} \dot{\mathbf{x}}(\text{grad}\Phi \cdot \mathbf{n}_{LG})dS \end{aligned} \quad (67)$$

Fig. 2 shows a potential profile across the section of a pore. According to the double-layer models [31], it has a shape similar to the concentration profile; that is, it is disturbed near the solid/liquid interface but tends to a flat profile toward the center of the pore. And like the concentration profiles shown on Fig. 3, increasing the ionic strength of the solution reduces the thickness of the area where the gradient of potential is different from zero. Accordingly, the integrals are neglected, assuming again that the electrical phenomena near the interface do not affect ionic movement. Eq. (67) thus simplifies to:

$$\overline{\text{grad}\psi}^L = \tau_L \text{grad}\overline{\psi}^L \quad (68)$$

Substituting Eq. (68) into (66) gives:

$$\overline{c_i \text{grad}\psi}^L = \overline{c_i}^L \tau_L \text{grad}\overline{\psi}^L \quad (69)$$

The same approach is used to average the chemical activity term in Eq. (60). The same assumptions concerning

the deviations, as well as those concerning the effect of the electrical phenomena at the solid/liquid interface, lead to:

$$\overline{c_i \text{grad}(\ln\gamma_i)}^L = \overline{c_i}^L \tau_L \text{grad}(\overline{\ln\gamma_i}^L) \quad (70)$$

It is assumed that the term $\overline{\ln\gamma_i}^L$ corresponds to the chemical activity coefficients calculated with the average concentrations $\overline{c_i}^L$. For simplicity, $\overline{\ln\gamma_i}^L$ is approximated by $\ln \overline{\gamma_i}^L$:

$$\overline{c_i \text{grad}(\ln\gamma_i)}^L = \overline{c_i}^L \tau_L \text{grad}(\ln \overline{\gamma_i}^L) \quad (71)$$

Finally, the advection term in Eq. (60) is averaged as:

$$\overline{c_i \mathbf{v}}^L = \overline{c_i}^L \overline{\mathbf{v}}^L + \overline{c_i^{\circ} \mathbf{v}}^L \quad (72)$$

The term in Eq. (72) containing the deviations is called the dispersive flux [13,34]. It is shown in the previous references that it can be written under a Fickian form:

$$\overline{c_i^{\circ} \mathbf{v}}^L = -D^{\text{disp}} \text{grad}c_i^L \quad (73)$$

where D^{disp} is called the coefficient of advective dispersion and is due to fingering, not diffusion. Consequently, this term can be added to the ionic diffusion term that would then exhibit a new diffusion coefficient being the sum of the classical one plus the coefficient of advective dispersion. When the fluid is in movement under the effect of a water content gradient, as described in the preceding section, the velocity is relatively weak. In that case, the dispersion term can be neglected [35], leading to:

$$\overline{c_i \mathbf{v}}^L = \overline{c_i}^L \overline{\mathbf{v}}^L \quad (74)$$

Substituting Eqs. (63), (69), (71), and (74) in Eq. (60) gives the average flux expression:

$$\begin{aligned} \theta_L \overline{\mathbf{j}_i}^L &= -D_i^{\mu} \theta_L \tau_L \text{grad}c_i^L - \frac{D_i^{\mu} z_i F}{RT} \theta_L \tau_L \overline{c_i}^L \text{grad}\overline{\psi}^L \\ &- D_i^{\mu} \theta_L \tau_L \overline{c_i}^L \text{grad}(\ln\overline{\gamma_i}^L) + \theta_L \overline{c_i}^L \overline{\mathbf{v}}^L \end{aligned} \quad (75)$$

The diffusion coefficient at the macroscopic level D_i is defined as:

$$D_i = \tau_L D_i^{\mu} \quad (76)$$

To simplify the expression, let:

$$C_i \equiv \overline{c_i}^L \quad (77)$$

$$\Psi \equiv \overline{\psi}^L \quad (78)$$

Substituting Eqs. (76) to (78) in Eq. (75) gives:

$$\begin{aligned} \theta_L \overline{\mathbf{j}_i}^L &= -D_i \theta_L \text{grad}C_i - \frac{D_i z_i F}{RT} \theta_L C_i \text{grad}\Psi \\ &- D_i \theta_L C_i \text{grad}(\ln\overline{\gamma_i}^L) + \theta_L C_i \overline{\mathbf{v}}^L \end{aligned} \quad (79)$$

Eq. (79) is now inserted in the averaged mass conservation Eq. (58) to yield the macroscopic ionic transport equation:

$$\begin{aligned} \frac{\partial(\theta_L C_i)}{\partial t} - \operatorname{div} \left(D_i \theta_L \operatorname{grad} C_i + \frac{D_i z_i F}{RT} \theta_L C_i \operatorname{grad} \Psi \right. \\ \left. + D_i \theta_L C_i \operatorname{grad}(\ln \bar{\gamma}_i^{-L}) - \theta_L C_i \bar{\mathbf{v}}^{-L} \right) + \theta_L \bar{r}_i^{-L} \\ + \frac{1}{V_o} \int_{S_s^L} \mathbf{j}_i \cdot \mathbf{n}_{LS} dS = 0 \end{aligned} \quad (80)$$

To simplify this equation, the integral must be expressed in a manner that is more friendly to a further numerical analysis. The term $(\mathbf{j}_i \cdot \mathbf{n}_{LS})$ gives the amount of ions crossing the solid/aqueous phase interface, as a result of dissolution/precipitation or ion exchange reactions. It is possible to express it differently by performing the averaging operation on the ions in the solid phase [13]. The conservation equation at the microscopic scale for the ions in solid phase is:

$$\frac{\partial c_{is}}{\partial t} + \operatorname{div}(\mathbf{j}_{is}) = 0 \quad (81)$$

where the subscript s designates the solid phase. Contrary to Eq. (52), it is assumed that no chemical reactions occur within the solid phase because all precipitation/dissolution phenomena are taking place at the solid/aqueous phase interface. Averaging Eq. (81) over the REV leads to:

$$\frac{\partial(\theta_s C_{is})}{\partial t} + \operatorname{div}(\theta_s \bar{\mathbf{j}}_{is}^{-s}) + \frac{1}{V_o} \int_{S_s^{SL}} \mathbf{j}_{is} \cdot \mathbf{n}_{SL} dS = 0 \quad (82)$$

where θ_s is the volumetric fraction of the solid phase and \mathbf{n}_{SL} is an outward (to the S phase) unit vector on the solid/ aqueous phase interface (designated as S^{SL}). The integral in Eq. (82) has the same value as the one in Eq. (80) but with an opposite sign because the ions coming out of the aqueous phase are being bound by the solid phase. Furthermore, the flux \mathbf{j}_{is} within the solid is zero because there is no ionic movement in this phase. This allows one to write:

$$\begin{aligned} \frac{\partial(\theta_s C_{is})}{\partial t} = -\frac{1}{V_o} \\ \times \int_{S_o^{SL}} \mathbf{j}_{is} \cdot \mathbf{n}_{SL} dS = \frac{1}{V_o} \int_{S_s^{SL}} \mathbf{j}_{is} \cdot \mathbf{n}_{SL} dS \end{aligned} \quad (83)$$

Substituting Eq. (83) in Eq. (80) gives:

$$\begin{aligned} \frac{\partial(\theta_L C_i)}{\partial t} - \operatorname{div} \left(D_i \theta_L \operatorname{grad} C_i + \frac{D_i z_i F}{RT} \theta_L C_i \operatorname{grad} \Psi \right. \\ \left. + D_i \theta_L C_i \operatorname{grad}(\ln \bar{\gamma}_i^{-L}) - \theta_L C_i \bar{\mathbf{v}}^{-L} \right) \\ + \theta_L \bar{r}_i^{-L} + \frac{\partial(\theta_s C_{is})}{\partial t} = 0 \end{aligned} \quad (84)$$

This is the general expression for the ionic transport in porous materials under isothermal conditions.

3.2. Coupling water and ionic transport

To model the transport of ions under the influence of capillary suction, it would seem straightforward to substitute Eq. (28) in Eq. (84). However, the development of the water transport equations was made for the case of pure water in a porous material. When ions are in solution, the vapor pressure above a solution is lower than in pure water [36]. This effect is quantified through Raoult's law. Accordingly, the relationship $\bar{p}_c = f(\theta_L)$ should instead be written as:

$$\bar{p}_c = f(\theta_L, c_i) \quad (85)$$

because the presence of ions in solution is likely to disturb the equilibrium between the aqueous and gaseous phases in a pore. To evaluate to what extent the presence of ions will affect the vapor pressure of water, one can use Raoult's law to calculate the vapor pressure change between pure water and a 500 mmol/l NaCl solution with water as solvent. According to Raoult's law [36], the vapor pressure change is given as:

$$\Delta p_v = X_{\text{solute}} p_v^o \quad (86)$$

where X_{solute} is the molar fraction of solute (NaCl) in the solution and p_v^o is the vapor pressure of pure water. At 25 °C, the vapor pressure of bulk water is 3.17 kPa [36]. Knowing that in 1 l of water there are 56 mol:

$$X_{\text{solute}} = \frac{0.5 \text{ mol NaCl}}{0.5 \text{ mol NaCl} + 56 \text{ mol water}} = 0.009 \quad (87)$$

This gives a change in vapor pressure of $\Delta p_v = 0.03$ kPa, which is obviously very weak. According to the result of this simple calculation, the effect of ionic concentration on the capillary pressure is neglected. It was also neglected in previous models presented in Refs. [23–25,28].

Substituting Eq. (28) in Eq. (84) gives:

$$\begin{aligned} \frac{\partial(\theta_L C_i)}{\partial t} - \operatorname{div} \left(D_i \theta_L \operatorname{grad} C_i + \frac{D_i z_i F}{RT} \theta_L C_i \operatorname{grad} \Psi \right. \\ \left. + D_i \theta_L C_i \operatorname{grad}(\ln \bar{\gamma}_i^{-L}) + C_i D_L \operatorname{grad} \theta_L \right) \\ + \theta_L \bar{r}_i^{-L} + \frac{\partial(\theta_s C_{is})}{\partial t} = 0 \end{aligned} \quad (88)$$

This equation can be used to model the transport of ions in unsaturated cement-based materials when the pore fluid is in movement because of capillary suction. To complete the model, an equation must be considered to evaluate the potential Ψ , as well as an expression to calculate the chemical activity coefficients. These topics are addressed in the following sections.

3.3. Calculation of the potential

The electrical potential in Eq. (88) arises in the material to enforce the electroneutrality condition. If two species are diffusing in a material, with one of the species having a greater self-diffusion coefficient, then in order to maintain a

neutral solution, the potential created slows the fastest ions and accelerates the slowest ones.

The mathematical relationship that relates electrical potential to electrical charge in a given medium is given by Poisson's equation [18]

$$\nabla^2 \psi + \frac{\rho}{\epsilon} = 0 \quad (89)$$

where ρ is the electrical charge density and ϵ is the medium permittivity. The charge density can be related to the ionic concentration through:

$$\rho = F \sum_{i=1}^N z_i C_i \quad (90)$$

where N is the number of ionic species. Substituting Eq. (90) in (89) gives:

$$\nabla^2 \psi + \frac{F}{\epsilon} \sum_{i=1}^N z_i C_i = 0 \quad (91)$$

It may seem awkward to have an equation from electrostatics in a model where the ions are moving through time. However, because the electromagnetic signal propagates much more rapidly than the ions do, Poisson's equation is perfectly suitable.

To use Eq. (91) in the transport model, it has to be averaged over the REV. As it was done previously, it is assumed that the boundary effects at the liquid/solid and liquid/gas interfaces are negligible. Following the same average rules as in the previous sections, we get the following relationship:

$$\text{div}(\theta_L \tau_L \text{grad} \Psi) + \theta_L \frac{F}{\epsilon} \sum_{i=1}^N z_i C_i = 0 \quad (92)$$

3.4. Evaluation of chemical activity coefficients

The models to calculate the chemical activity coefficients are numerous. The first ones developed are the Debye–Hückel and extended Debye–Hückel models [37]. From purely electrostatic considerations, they relate the chemical activity coefficients of ionic species to the ionic strength of a solution. They are valid for ionic strengths up to 10 and 100 mmol/l, respectively.

In cement-based materials, the ionic strength is much higher. To suit this particular situation, a chemical activity relationship was developed recently by Samson et al. [38], which gives good results for highly concentrated solutions:

$$\ln \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + \frac{(0.2 - 4.17 \times 10^{-5} I) Az_i^2 I}{\sqrt{1000}} \quad (93)$$

where I is the ionic strength of the solution, and A and B are temperature-dependent parameters. The parameter a_i in Eq. (93) varies with the ionic species considered.

3.5. Modeling of chemical reactions

Two terms appear in Eq. (84) to account for chemical reactions. The term \bar{r}_i^L is a sink/source term that models homogeneous chemical reactions [39], i.e., reactions that solely involve the aqueous phase, as for instance:



The other term related to chemical reactions is $\partial(\theta_s C_{is})/\partial t$. As mentioned before, it accounts for ionic exchanges between the aqueous and solid phases. This type of chemical reaction is called heterogeneous [39]. It includes dissolution/precipitation and surface exchange phenomena. The formation of portlandite is an example of heterogeneous reaction:



In most cases, chemical reactions are modeled by assuming that they are faster than ionic transport. A dimensional analysis by Barbarulo et al. [40] showed that this local equilibrium assumption (LEA) is valid in most situations for ionic transport in cementitious materials. Under LEA, chemical reactions are modeled by algebraic mathematical relationships [39]. Following a paper published in 1989 by Yeh and Tripathi [41], the current trend for solving ionic transport problems in reactive materials is to separate the transport and chemical reaction parts. The partial differential equations describing ionic transport are solved with the finite difference or finite element method, whereas a Newton algorithm is used to solve the nonlinear algebraic system of equation associated with the chemical reactions. Depending on the type of chemical reactions involved in a problem, different algorithms can be used to split transport and chemistry, as reviewed in Refs. [42,43].

When the local equilibrium assumption is not valid, chemical reactions are modeled with kinetic expressions [39] involving reaction rate. This case arises for problems in groundwater ionic transport where large pressure head gradients can be at the origin of high fluid velocity. Kinetically controlled reaction modeling is discussed in Refs. [44–46].

3.6. Evaluation of the ionic transport properties

Two different transport parameters appear in Eq. (88). There is the diffusion coefficient D_i associated with the diffusion process and the liquid water diffusivity D_L to characterize the effect of the fluid velocity on the ionic transport. A discussion of D_L was already given in Section 2.5.

The diffusion coefficient is evaluated with the migration experiment test. It consists in accelerating chloride ions with an applied external potential through a disk of cement-based materials glued between two cells filled with ionic solutions. The analysis of the results yields the diffusion coefficients. Different analysis methods are found in the literature. One is

based on steady-state measurements of chloride having crossed the sample [47,48]. Another [49] is based on measuring non-steady-state chloride profiles by grinding the sample after a short exposure. A recent paper by Samson et al. [50] describes a method based on current measurements during the migration test. The measurements are analyzed with the extended Nernst-Planck model to yield the diffusion coefficient of each ionic species in the material.

All these methods are performed in saturated conditions. As shown in Eq. (76), the diffusion coefficient D_i depends, through τ_L , on the saturation condition. No method could be found in the literature to evaluate this parameter for unsaturated conditions. However, it is possible that D_i might not be affected by the saturation state of the material above a given saturation level, the latter being defined as $s = \theta_L / \phi$, where ϕ is the porosity. Revil [32] showed that for shaly sand, the diffusion of the ions is almost unaffected for a water saturation above 0.6. We thus infer that for concrete structures exposed to high relative humidity environment, the diffusion coefficient is independent of the water content.

In the flux Eq. (75), the recurring quantity $\tau_L \theta_L$, which could also be written $\tau_L s \phi$, is analogous to a saturation-dependent formation factor for the liquid phase of the pore system. The saturation s results from the averaging over the REV. The tortuosity τ_L is also a function of the saturation and reflects the connectedness of the moisture phase. At a critical moisture content s_c , the liquid phase is no longer connected, the tortuosity τ_L goes to zero, and the transport within the liquid phase ceases.

The remaining question is the dependence of the tortuosity τ_L on the saturation. Although no precise data exist for cementitious systems, there exist qualitative data from which inferences can be made. These data typically express the relative total conduction as a function of the saturation s . The relative total conduction σ / σ_o is analogous to the product of the saturation and the relative tortuosity:

$$\frac{\sigma(s)}{\sigma(s=1)} = \frac{s\tau_L(s)}{\tau_L(s=1)} = \frac{s\tau_L}{\tau_{Lo}} \quad (96)$$

Therefore, dividing these results by s will yield the relative change in the tortuosity.

The work of Martys [19] suggests that, for a preferentially wetting liquid being displaced by a nonwetting one, the limiting behavior of τ_L near saturation can be approximated by the dilute effective medium theory result:

$$\frac{s\tau_L}{\tau_{Lo}} = 1 - \frac{3}{2}(1-s) + \frac{1}{2}(1-s)^2 \quad s \rightarrow 1 \quad (97)$$

(Here, the more exact coefficient of 0.558 for the quadratic term has been roughly approximated by 1/2.) The relative tortuosity can be solved for algebraically:

$$\frac{\tau_L}{\tau_{Lo}} = \frac{s}{2} + \frac{1}{2} \quad (98)$$

Therefore, a decrease to 80% saturation will result in a 10% change in the tortuosity. Given that transport coefficients can routinely change by orders of magnitude, a 10% change in the tortuosity is relatively quite minor. Because this result is only approximate near saturation, further reductions in saturation would have a far greater effect.

4. Conclusion

The mathematical model developed in this paper is first summarized. For materials where the water transport occurs as a result of capillary suction, the water content profile can be calculated with Richards' Eq. (51). The ions will move in the material under the combined effect of diffusion (including electrical and activity effects) and water movement according to Eq. (88). The electrical potential, arising from the electrical coupling between the ions to maintain a neutral solution, is calculated with Poisson's Eq. (92). The chemical activity coefficients, for the highly charged pore solution of cement-based materials, can be evaluated with Eq. (93). Finally, several references were given to address the modeling of chemical reactions occurring in cementitious materials.

The use of the averaging technique clearly helps to clarify the meaning of some important parameters in the model. According to this technique, the water content in Richards' model corresponds to a volumetric water content. The water diffusivity was clearly shown to be a contribution of both liquid water and vapor transport. The diffusion coefficient, the parameter that characterizes the ionic diffusion process, is directly related to the geometrical properties of the material through a parameter called the tortuosity.

The averaging technique proved to be a powerful mathematical tool to lay the foundation of transport models in porous media.

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