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ABSTRACT

Migration tests are now commonly used to estimate the diffusion coefficients of cement-based materials. Over the past decade, various approaches have been proposed to analyze migration test results. In many cases, the interpretation of test data is based on a series of simplifying assumptions. However, a thorough analysis of the various transport mechanisms that take place during a migration experiment suggests that some of them are probably not valid. Consequently, a more rigorous approach to analyze migration test results is presented. The test procedure is relatively simple and consists in measuring the evolution of the electrical current passing through the sample. Experimental results are then analyzed using the extended Nernst-Planck-Poisson set of equations. A simple algorithm is used to determine for each experiment the tortuosity factor that allows to best reproduce the current curve measured experimentally. The main advantage of this approach resides in the fact that the diffusion coefficients of all ionic species present in the system can be calculated using a single series of data. Typical examples of the application of this method are given. Results indicate that the diffusion coefficients calculated using this approach are independent of the applied voltage and depends only slightly on the concentration level and the chemical make-up of the upstream cell solution.

RÉSUMÉ

Les essais de migration sont maintenant couramment utilisés pour estimer les coefficients de diffusion des matériaux cimentaires. Récemment, différentes approches ont été proposées pour analyser les résultats de l'essai de migration. Dans la plupart des cas, l'analyse des mesures est basée sur une série d'hypothèses simplificatrices. Cependant, une étude détaillée des mécanismes de transport des ions présents durant l'essai de migration révèle que certaines de ces hypothèses sont probablement incorrectes. Une approche plus rigoureuse de l'analyse des résultats de l'essai de migration est donc présentée. La méthode consiste à mesurer les courants électriques traversant l'échantillon durant l'essai. Ces résultats sont ensuite analysés à l'aide du système d'équations Nernst-Planck − Poisson. Un algorithme numérique permet de trouver pour chaque essai le facteur de tortuosité permettant de reproduire au mieux la courbe de courant mesurée expérimentalement. L'avantage principal de cette méthode est qu'elle permet de calculer le coefficient de diffusion de chacune des espèces ioniques présente dans le matériau sur la base de cette seule mesure de courant. Des exemples d'utilisation de la méthode sont décrits. Les résultats montrent que les coefficients de diffusion évalués selon cette approche sont indépendants du voltage appliqué au cour de l'essai et qu'ils ne dépendent que très légèrement du niveau de concentration et du type de solution utilisé dans le bac amont du montage.

1. INTRODUCTION

Concrete durability is a growing concern that continues to consume an increasing amount of public funds allocated for repairing civil engineering infrastructures throughout the world. In this context, service life modeling has become

a subject of focused research activity. Considerable effort has been expended in the development of service life models for predicting the long-term behavior of concrete structures. These models have been developed to improve concrete performance and to facilitate future repair planning strategies.

One approach to service life modeling of concrete structures is based on the detailed description of ionic transport mechanisms and chemical equilibrium within the hydrated cement paste fraction of the material [1, 2]. Models to predict the transport of ions in concrete pore solution and the corresponding chemical reactions are complex. Consequently, accurate transport models require a sound understanding of the various physical and chemical phenomena involved. Accordingly, research on the subject has flourished and experimental methods to properly evaluate the various parameters found in the mathematical models have been significantly improved.
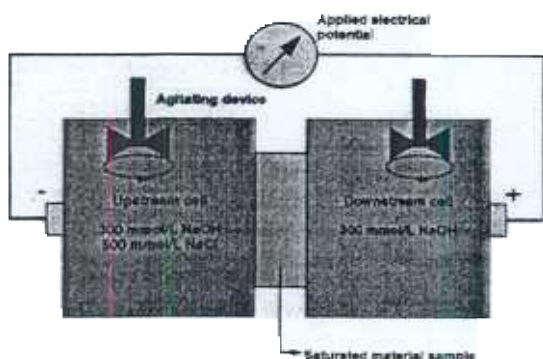

Fig. 1 - Typical set-up for the migration test.

For the majority of field concrete failure mechanisms, the critical chemical reaction depends upon the diffusive transport of ionic species. Therefore, one of the critical parameters characterizing the movement of ions is the diffusion coefficient. Historically, this parameter was determined using the divided cell diffusion set-up (see Fig. 1) [3, 4]. Unfortunately, diffusion experiments tend to be very time consuming. In many instances, ions may take several months (even up to a year in certain cases) to penetrate a 1 cm thick disc of mortar [4, 5].

Over the past decades, numerous attempts to design accelerated test procedures have been made. In most cases, an experimental set-up similar to the one utilized for a diffusion experiment (see Fig. 1) is used but the transport of ions through the samples is accelerated by the application of an electrical potential to the system. These accelerated diffusion experiments, currently called migration tests, are now commonly used to characterize the ionic diffusion properties of hydrated cement systems.

Various versions of the migration test have been developed. These different procedures can be divided into two categories. In steady-state migration experiments, the evolution of the concentration of a given ionic species (in many cases chloride ions) in the downstream compartment of the cell is monitored for a few days [6, 7]. In non-steady state migration tests, the depth of ion penetration within the sample (or alternatively the current passing through the sample) is measured after a given period [8-10].

Despite these variations, all migration tests share some common features. Experiments are usually performed on fully saturated samples, and test solutions are typically maintained at a pH over 12.5 in order to preserve, as much as possible, the microstructure of the material during the test. In addition, the electrical potential applied on the system ranges from 400 to 1200 V/m. Comprehensive critical reviews of the various migration test procedures used to investigate the transport properties of concrete can be found in references [4, 11].

Numerous aspects of the migration tests have been investigated. For instance, it is now well established that the transport of ions (hence migration test results) is quite sensitive to temperature variations of the cell [4,12,13]. These investigations have clearly emphasized the importance of conducting migration experiments under isothermal conditions. Various approaches to calculate diffusion coefficients on the basis of migration test results have also been proposed [4]. Although these studies have improved knowledge on the fundamental mechanisms involved in a migration experiment, some of them have also raised questions on the relative influence of parameters such as the nature and concentration of the test solution and the intensity of the electrical potential applied on the cell during the experiment. However, recent numerical developments have cast some doubts on the hypotheses at the basis of some of these calculation methods. This paper attempts to shed some new light on the analysis of isothermal migration test results.

2. DESCRIPTION OF IONIC TRANSPORT MECHANISMS IN REACTIVE POROUS MEDIA

In (unsaturated) porous materials, the movement of ions takes place in the liquid phase that occupies a fraction of the total porous volume. It occurs as a combination of diffusion and advection (i.e. fluid movement). Since ions are charged particles, their movements in solution is affected by the presence of other ionic species through an electrical coupling. The transport of ions may also be affected by the various chemical reactions that may occur within the material. Ions can react with other species present in the pore solution to form new compounds. They can also interact with other ions found in the double layer at the surface of the pores, or eventually be bound to the various solid phases forming the skeleton of the porous material.

In hydrated cement systems, all the above phenomena are bound to occur. Electrical effects tend to be particularly significant since the pore solution is highly concentrated. The chemical reactions can also be very important since some of the solid phases of the cement paste are very reactive, particularly the ones that are alumina-based [14, 15].

2.1 Mathematical treatment of transport phenomena

Previous work has shown that it is possible to model the transport of ions by averaging the extended Nernst-Planck equation with an advection term [16] over a Representative Elementary Volume (REV). Details on the averaging

technique can be found elsewhere [17, 18]. This yields the following transport equation [19] (given here for 1D cases) that should be written for each ionic species present in the system:

$$\frac{\partial\left(\theta_s C_{is}\right)}{\partial t}+\frac{\partial\left(\theta C_i\right)}{\partial t}-\frac{\partial}{\partial x}\left(\theta D_i\frac{\partial C_i}{\partial x}\right.$$
$$\left.+\theta\frac{D_i z_i F}{RT}C_i\frac{\partial \Psi}{\partial x}+\theta D_i C_i\frac{\partial\ln\gamma_i}{\partial x}-C_i V_x\right)=0 \quad (1)$$

The uppercase symbols represent averaged quantities: C_i is the concentration of the ionic species i, C_{is} is the concentration of the species i in solid phase, θ_s is the volumetric solid content of the material, θ is the volumetric water content in the pores, Ψ is the electrical potential, D_i is the diffusion coefficient, z_i is the valence number of the species, F is the Faraday constant, R is the ideal gas constant, T is the absolute temperature of the liquid, γ_i is the chemical activity coefficient and V_x is the bulk velocity of the fluid. The bulk ionic flux J_i is given by:

$$J_i=-\theta D_i\frac{\partial C_i}{\partial x}-\theta\frac{D_i z_i F}{RT}C_i\frac{\partial \Psi}{\partial x}$$
$$-\theta D_i C_i\frac{\partial\ln\gamma_i}{\partial x}+C_i V_x \quad (2)$$

In Equations (1) and (2), the diffusion coefficient D_i is defined as:

$$D_i=\tau D_i^\mu \quad (3)$$

where τ is the tortuosity of the material and D_i^μ is the diffusion coefficient of the species i in free water, which

Table 1 – Diffusion coefficient of various species in free water

Species	D_i^μ (10^{-9} m^2/s)
OH$^-$	5.273
Na$^+$	1.334
K$^+$	1.957
SO$_4^{2-}$	1.065
Ca^{2+}	0.792
Cl$^-$	2.032
Mg^{2+}	0.706

values can be found in physics handbooks (see for instance reference [20]). Values of D_i^μ for the most common species found in cement-based materials are given in Table 1. The values of D_i^μ appearing in Table 1 are constant and represent the diffusion coefficients in very dilute conditions.

The tortuosity appears in the model as a result of the averaging procedure [17, 18]. It characterizes the intricacy of the path that ions must travel in a given porous material. Equation (3) has very important implications. For instance, it shows that if the diffusion coefficient D_i of one ionic species is known, τ is also known and, accordingly, the diffusion coefficient of each of the other ionic species can be easily calculated. It also shows that as long as the tortuosity of the material remains unchanged, each D_i is constant.

To evaluate the electrical potential Ψ, Poisson's equation [16, 21] must be solved simultaneously with Equation (1). Poisson's equation relates the electrical potential Ψ to the electrical charge $\sum_i z_i C_i$ in solution. It is given here in its averaged form [18, 19]:

$$\frac{d}{dx}\left(\theta\tau\frac{d\Psi}{dx}\right)+\theta\frac{F}{\varepsilon}\sum_{i=1}^N z_i C_i=0 \quad (4)$$

where N is the total number of ionic species and ε is the dielectric permittivity of the media. In this study, the permittivity is assumed to be the same as that of water.

To calculate the chemical activity coefficients, several approaches are available. Models such as those proposed by Debye-Hückel or Davies are unable to reliably describe the thermodynamic behavior of highly concentrated electrolytes such as the hydrated cement paste pore solution. A modification of the Davies equation was found to yield good results [22]:

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

where I is the ionic strength of the solution, and A and B are temperature dependent parameters. The parameter a_i in Equation (5) varies with the ionic species considered.

As noted previously, the variable V_x appearing in Equation (1) stands for the fluid phase flux. In cement-based materials, the fluid will often be in movement as a result of capillary forces arising from the wetting and drying cycles to which the material is exposed. In these cases, the fluid flux can be expressed as [23]:

$$V=-D_L\frac{\partial\theta}{\partial x} \quad (6)$$

where D_L is the non-linear liquid water diffusivity coefficient. Water content profiles in the material can be evaluated on the basis of Richard's equation [23], which is given by:

$$\frac{\partial\theta}{\partial t}-\frac{\partial}{\partial x}\left(D_w\frac{\partial\theta}{\partial x}\right)=0 \quad (7)$$

where D_w is the global water diffusivity coefficient, taking into account water molecules under both vapor and liquid phase. Equation (7) is also known as Fick's second law.

2.2 Mathematical treatment of chemical reactions

In hydrated cement systems, chemical reactions are bound to occur during the transport of ions, whether there is an applied field or not. If there is no electrical field, the rate of transport of ions is slow compared to the kinetics of the various chemical reactions [24]. Since the evolution of the microstructure of the material is essentially controlled by the rate of transport of ions, the equilibrium of the system is considered to be *locally* maintained.

If the local equilibrium is maintained, several methods for modeling the chemical reactions can be used, as reviewed in reference [25]. A technique often used is to

experimentally determine an interaction isotherm that gives a relationship between the solids concentrations C_{is} and solute concentration C_i [26]. This relationship is then directly inserted in Equation (1). Although relatively straightforward, this method is limited by the fact that it can hardly take into account the influence of numerous ionic species on the equilibrium of a given solid phase with the surrounding pore solution. This is the reason why many authors have elected to rely on a different approach and model chemical reactions using a chemical equilibrium code [19, 25, 27, 28].

During a migration test, the situation is significantly different. A dimensional analysis of the problem indicates that the local chemical equilibrium is usually not respected during a migration experiment [29]. This can be explained by the fact that the application of a difference in potential of 400 V/m results in a rate of ionic transport that is much faster than the kinetics of chemical reaction. The dimensional analysis also demonstrates that, in most migration experiments, chemical reactions have little influence on the local ionic concentration within the test sample[1].

Since the local equilibrium is not maintained during migration experiments, the models reviewed in reference [25] are no longer appropriate. Relatively little research has been dedicated to the treatment of these non-equilibrium problems in hydrated cement systems. Rubin [30] gives a general framework to model these reactions. According to this approach, the non equilibrium reaction for a solid $\overline{M_1M_2}$ in contact with the ions M_1 and M_2, found in concentrations c_1 and c_2 respectively, is expressed as:

$$\overline{M_1M_2} \underset{k_b}{\overset{k_a}{\Longleftrightarrow}} M_1 + M_2 \qquad (8)$$

where k_a and k_b are the reaction rate coefficients associated with the dissolution and precipitation, respectively. The rate of formation of ions M_1 and M_2 into solid phases can be expressed as [30]:

$$\frac{\partial c_{1s}}{\partial t} = \frac{\partial c_{2s}}{\partial t} = -k_a c_1 c_2 + k_b \qquad (9)$$

which could be inserted directly in Equation (1). The problem, however, is to determine k_a and k_b, which are likely to be related to the solute concentration and to the applied external voltage, since it determines the velocity of the ions. To our knowledge, no systematic data on this topic have been published. Recent work by Castellote et al. [31] has emphasized the complexity of these problems.

3. MODELING OF IONIC TRANSPORT DURING MIGRATION TESTS

The mathematical model described previously can be used to model the transport of ions in various cases (e.g. external chemical attack, leaching problems, ...). For the

specific case of the migration test, some simplifications can be made. Migration tests are performed in saturated conditions, and no pressure gradient is applied on the liquid phase. Accordingly, the advection term in Equation (1) can be dropped, as well as Richard's equation (Equation (7)). Furthermore, the fact that the material is maintained in saturated conditions allows simplifying the expression relating porosity ϕ and volumetric water content θ:

$$\theta = \phi \qquad (10)$$

$$\theta_s = 1 - \phi$$

These assumptions may be used to simplify Equation (1):

$$\frac{\partial\left((1-\phi)C_{is}\right)}{\partial t} + \frac{\partial(\phi C_i)}{\partial t} - \frac{\partial}{\partial x}\left(\phi D_i \frac{\partial C_i}{\partial x}\right.$$
$$\left. + \phi \frac{D_i z_i F}{RT} C_i \frac{\partial\Psi}{\partial x} + \phi D_i C_i \frac{\partial \ln\gamma_i}{\partial x}\right)$$

Similarly, the ionic flux of Equation (2) can now be written as:

$$J_i = -\phi D_i \frac{\partial C_i}{\partial x} - \phi \frac{D_i z_i F}{RT} C_i \frac{\partial\Psi}{\partial x} - \phi D_i C_i \frac{\partial \ln\gamma_i}{\partial x} \qquad (13)$$

In most papers dealing with the analysis of migration test data, it is assumed that chemical reactions can be neglected. This hypothesis is, at least partially, justified by the fact that non steady-state migration tests have a shorter duration than steady-state experiments. In addition, as previously discussed, the high velocity of the ions being transported through the pore structure of the material tends to greatly attenuate the influence of chemical reactions. Neglecting the chemical reactions also implies that there is no change to the microstructure of the paste during the duration of the test, which is equivalent to assuming that the porosity and tortuosity remain constant. Following this assumption, Equation (12) can be simplified as:

$$\frac{\partial C_i}{\partial t} - \frac{\partial}{\partial x}\left(D_i \frac{\partial C_i}{\partial x} + \frac{D_i z_i F}{RT} C_i \frac{\partial\Psi}{\partial x} + D_i C_i \frac{\partial \ln\gamma_i}{\partial x}\right) = 0 \qquad (14)$$

These assumptions also yields a simplified version of the averaged Poisson's equation:

$$\tau \frac{d^2\Psi}{dx^2} + \frac{F}{\varepsilon}\sum_{i=1}^{N} z_i C_i = 0$$

The set of N equations (14), combined with Equation (15) for the electrical potential and Equation (5) for the chemical activity coefficients, has to be solved in order to model the transport of ions in saturated materials during a migration test. This coupled system of equation can be solved using the finite element method. Information on a numerical algorithm that has been specifically developed for the resolution of these problems can be found in references [32, 33].

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[1] These conclusions are valid for ordinary concrete mixtures for which the water/binder ratio is 0.40 or higher. These conclusions are probably not valid for high-performance concrete mixtures.

4. A FURTHER SIMPLIFICATION - THE CONSTANT FIELD ASSUMPTION

Despite the various simplifications discussed in the previous section, solving the previous system of equations can be relatively complicated. This is the reason why numerous attempts have been made to further simplify the analysis of migration test results. The various approaches proposed in the literature can be roughly divided into two groups: those directly related to the treatment of steady-state migration test results and those associated to the analysis of non steady-state test data[2]. Consequently, these two different families of simplifications will be reviewed separately.

4.1 Steady-state migration experiments

During a transport experiment, the steady-state regime is reached when the concentration of the species under consideration (*e.g.* chloride) in the downstream compartment of the cell (see Fig. 1) varies linearly with respect to time. This indicates a constant flux, which is the basic definition of the steady-state. It implies that all chemical reactions are completed. As previously emphasized, in classical diffusion experiments performed on representative concrete samples, it usually takes a very long time to establish the steady-state. However, in migration tests, the constant flux is often reached in a few days.

From the standpoint of modeling, the treatment of steady-state problems is relatively simple since all time-dependent terms appearing in Equation (14) are set equal to zero. This is equivalent to solving the flux equation (Equation (13)) with J_i being constant.

To further simplify the analysis, it is assumed that the external voltage is sufficiently strong to overwhelm all the other terms in the flux equation [34-37]. This means that the diffusion, chemical activity effects and electrochemical coupling between the ions are neglected. This simplification allows to consider a linear variation of the electrical potential in the sample:

$$\frac{\partial \Psi}{\partial x} = \frac{\Delta \Psi_{ext}}{L} = -E_{ext} = \text{constant} \qquad (16)$$

where $\Delta \Psi_{ext}$ is the difference in voltage applied across the sample, L is the thickness of the specimen, and E_{ext} is the corresponding constant electric field. Equation (16) is known as the constant field assumption. In that case, Equation (13) reduces to:

$$J_i = -\phi \frac{D_i z_i F}{RT} C_i \frac{\Delta \Psi_{ext}}{L} \qquad (17)$$

where J_i is a constant since steady-state is reached.

The knowledge of the chloride flux allows to calculate D_i from Equation (17). This approach was used in references [34-37]. In reference [37], an equation similar to (17) is used, but an empirical correction factor accounting for activity effects is applied.

4.2 Non steady-state migration experiments

In an attempt to determine chloride diffusion coefficient, Tang and Nilsson [38] proposed an analysis of migration test results based on non steady-state measurements. According to Tang and Nilsson's approach [38], the potential gradient across the sample is assumed to be constant and corresponds to the externally applied electrical field. Chemical activity effects are also neglected. Following these hypotheses, Equation (12) reduces to:

$$\frac{\partial C_i}{\partial t} - \frac{\partial}{\partial x}\left(D_i \frac{\partial C_i}{\partial x} - \frac{D_i z_i F}{RT} C_i E_{ext} \right) = 0$$

For semi-infinite media, the analytical solution of Equation (18) with a constant D_i is:

$$C = \frac{C_o}{2}\left[\text{erfc}\left(\frac{x}{2\sqrt{D_i t}} - \frac{z_i F E_{ext}\sqrt{D_i t}}{2RT} \right) \right.$$
$$\left. + e^{\left(\frac{z_i F E_{ext}}{RT} x \right)} \text{erfc}\left(\frac{x}{2\sqrt{D_i t}} + \frac{z_i F E_{ext}\sqrt{D_i t}}{2RT} \right) \right]$$

where C_o is the boundary condition at $x=0$.

According to this approach, the value D_i is obtained by fitting the chloride profile calculated numerically (*i.e.* from Equation (18)) to the one measured during the migration test. Experimental chloride profiles are usually obtained by milling at the end of the experiment the test sample over several depth increments[3]. The powder samples are then tested for acid-soluble chlorides in accordance with ASTM C1152. Alternatively, the test sample can be splitted into two pieces. The total depth of penetration is then estimated using a colorimetric method (see for instance reference [8]).

4.3 Discussion on the validity of the constant field hypothesis

Over the years, numerous authors have investigated the use of Equations (17) and (18) to calculate diffusion coefficients on the basis of migration test data. Many
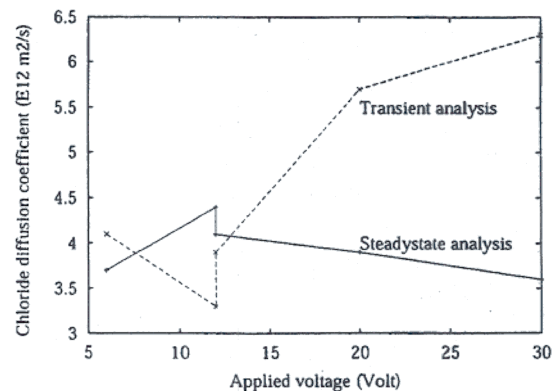
Fig. 2 – Influence of voltage determination on diffusion coefficients: comparison of two analysis method (data from reference [35]).

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[2] *This last category includes most conduction experiments for which the test period is limited to a few hours.*

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[3] *Each increment is typically a few millimeters in depth.*

Table 2 - Data for the non steady-state chloride migration simulation.	
Properties	Values
Thickness	35 mm
Tortuosity	0.01
Porosity	0.11
Diffusion coefficients	$(10^{-11}\ m^2/s)$
OH⁻	5.27
Na⁺	1.33
K⁺	1.96
SO₄²⁻	1.06
Ca²⁺	0.79
Cl⁻	2.03
Initial conditions	
OH⁻	400.0 mmol/L
Na⁺	100.0 mmol/L
K⁺	320.0 mmol/L
SO₄²⁻	11.0 mmol/L
Ca²⁺	1.0 mmol/L
Cl⁻	0.0 mmol/L
Ψ	0.0 V
Boundary cond. (x=0)	
OH⁻	300.0 mmol/L
Na⁺	800.0 mmol/L
K⁺	0.0 mmol/L
SO₄²⁻	0.0 mmol/L
Ca²⁺	0.0 mmol/L
Cl⁻	500.0 mmol/L
Ψ	0.0 V
Boundary cond. (x=L)	
OH⁻	300.0 mmol/L
Na⁺	300.0 mmol/L
K⁺	0.0 mmol/L
SO₄²⁻	0.0 mmol/L
Ca²⁺	0.0 mmol/L
Cl⁻	0.0 mmol/L
Ψ	14.0 V
Temperature	25°C

The apparent sensitivity of diffusion coefficient values calls into question the validity of Equations (17) and (18). As previously mentioned, D_i should be an *instrinsic property* of the material (and of the ionic species considered). Accordingly, its value should be independent of the boundary conditions used during the test (at least for migration experiments performed under isothermal conditions).

The significant variations of D_i with the concentration of the test solution and the voltage applied to the system can be, at least partially, explained by the fact that Equations (17) and (18) were both developed on the basis of the constant field assumption. Although the validity of this hypothesis has been discussed by various authors in the past [40-43], the question has apparently never been settled.

In order to validate the constant field assumption, a sample problem is studied. It consists in calculating the penetration of chloride ions within a sample during a migration test with three different transport models:

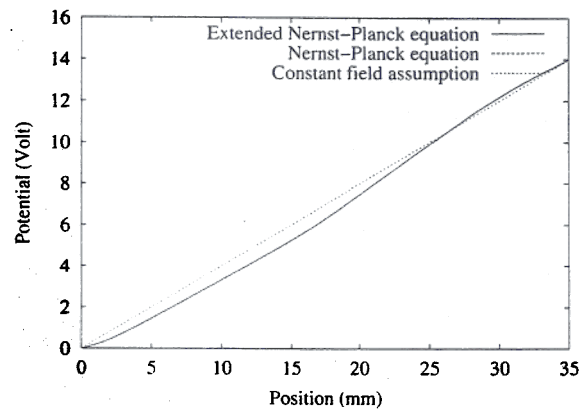• Extended Nernst-Planck equation coupled with Poisson's equation (Equations (14) and (15))

Fig. 3 – Sample problem: Comparison of the electrical potential in the material after 20 h for the different models: extended Nernst-Planck (Equation (14), Nernst-Planck (Equation (14) without the activity term), constant field assumption (Equation (19)).
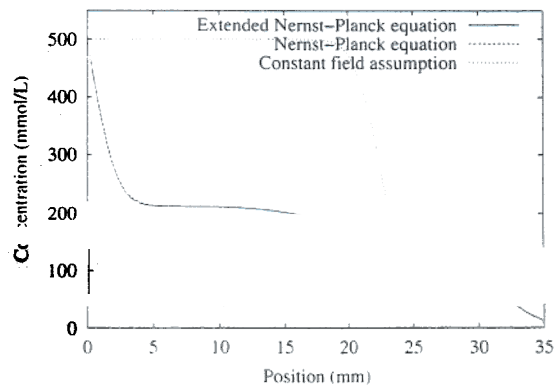

Fig. 4 - Sample problem: Comparison of the chloride profiles in the material after 20 h for the different models: extended Nernst-Planck (Equation (14)), Nernst-Planck (Equation (14) without the activity term), constant field assumption (Equation (19)).

authors have found the diffusion coefficients derived from both equations to be sensitive to the boundary conditions. For instance, in a very comprehensive analysis of steady-state chloride migration experiments, Hauck [39] observed quite significant variations of D_i according to the concentration of the test solution in the upstream compartment. Similar results were later reported by Zhang and Gjørv [37].

In another series of migration experiments performed on samples of a 0.5 water/cement ratio concrete, McGrath and Hooton [35] investigated the influence of voltage on both the steady-state and non steady-state regimes. Their results are summarized in Fig. 2. As can be seen, the applied potential was found to have a strong influence of the values of D_i. This is particularly the case for the diffusion coefficients calculated using Equation (18), *i.e.* those obtained for the non steady-state migration experiments for which D_i values were found to vary by a factor of two.

Table 3 – Steady state flux calculation for the three different ionic transport model.	
Model	Flux (mol/m^2/s)
Extended Nernst-Planck	7.5×10^{-6}
Nernst-Planck	7.6×10^{-6}
$J_i = -\phi \dfrac{D_i z_i F}{RT} C_i \dfrac{\Delta \Psi_{ext}}{L}$	1.7×10^{-5}

- Nernst-Planck equation coupled with Poisson's equation (Equation (14) without the chemical activity term and Equation (15))
- Constant field assumption without chemical activity effects (Equation (19)).

In all cases, it was assumed that a 35 mm thick concrete sample was subjected to a electrical potential of 14 V. The data needed to perform the calculations are given in Table 2. All calculations were done over a 20 h period.

The electrical potential distributions obtained from the resolution of the three different sets of equations after 20 h of test are shown in Fig. 3. The figure reveals only slight differences between the potential profile predicted by the constant field assumption (*i.e.* Equation (18)) and that predicted by the two versions of the extended Nernst-Planck equations (*i.e.* Equations (14) with and without the chemical activity term). However, the slight differences in potential profiles lead to significant differences in chloride concentration profiles, as shown in Fig. 4. As can be seen, the constant field assumption has not only a significant influence on the total depth of chloride penetration but it also markedly influences the distribution of ions across the entire sample. According to Equation (19), chloride ions do penetrate the sample as a relatively sharp front, while the two profiles predicted by Equations (14) and (15) are much more similar to those observed for a simple diffusion experiment. Results appearing in Fig. 4 also indicate that chemical activity effects have little influence on the concentration profile during a non steady-state migration test.

Typical non steady-state migration test results previously reported by Tang and Nilsson [9] are given in Fig. 5. These profiles are similar in shape to those usually found in the literature for non steady-state migration tests (see for instance reference [8]). The comparison of these two profiles to those appearing in Fig. 4 illustrates the inherent
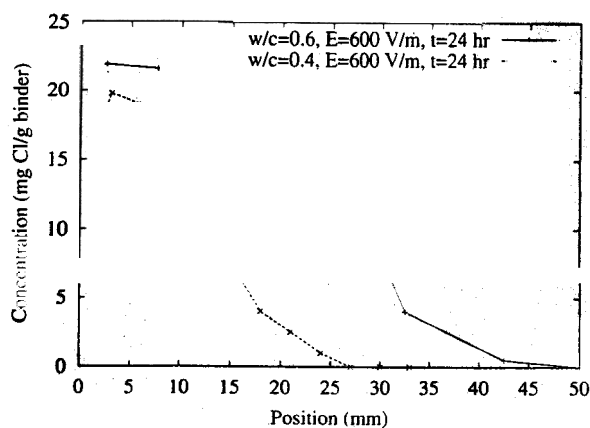
difficulty of calculating diffusion coefficients using Equation (19). As mentioned in the previous section, the value D_i is obtained by fitting the chloride profile calculated numerically to the one measured during the migration test. Given the marked difference between the shapes of the two curves, it is hard to see how the resolution of Equation (18) can yield reliable diffusion coefficient values.

A comparison was also made between the steady-state flux calculated with the extended Nernst-Planck model (Equation (14)), Nernst-Planck model (Equation (14) without the chemical activity term), and the simplified steady state model (Equation (17)). Results are given in Table 3. On the one hand, the steady-state results show that the chemical activity gradient has only a minor influence on the transport of ions during the test. On the other hand, the simplified steady-state model overestimates the kinetics of transport of ions. The flux of chlorides calculated with the simplified model is 2.7 times higher than the one calculated with the extended

Nernst-Planck model. These results are in good agreement with the observations made by various authors who found that diffusion coefficients calculated using a constant-field assumption are usually higher than those derived from the analysis of simple diffusion experiments [8, 44, 45].

5. AN ALTERNATIVE APPROACH TO CALCULATE DIFFUSION COEFFICIENTS USING MIGRATION TEST RESULTS

The numerous advantages of using the Nernst-Planck/Poisson set of equations to analyze migration test results have been clearly illustrated in the previous section. Over the past years, a more systematic application of this approach has been developed and tested on both laboratory and field concrete samples. This method is briefly described in the following sections.

5.1 Description of the experimental procedure

The experimental method used to test the samples is essentially a non steady-state migration experiment and can be considered as a modified version of the ASTM C1202 procedure. Two representative samples (100 mm in diameter) are usually tested per mixture. The thickness of the samples ranges from 25 mm for mortars to 50 mm for concrete mixtures. The samples are vacuum saturated in a 300 mmol/L NaOH solution prior to testing. The disks are then glued to plastic rims that fit between the upstream and the downstream cell (see Fig. 1), leaving an exposed diameter of about 76 mm.

Both compartments of the migration cell are filled with a sodium hydroxide solution prepared at a pH of 13.5. As previously mentioned, the high pH of the test solutions contributes to minimize the risk of microstructural alterations during the experiment. The upstream compartment also contains another salt, like NaCl or Na_2SO_4. The transport of ions through the sample is accelerated by applying an electrical potential (usually 500 V/m) across the two surfaces of the sample. The current passing through the system and the chloride concentration of the downstream compartment are monitored during

Fig. 5 - Chloride profiles measured by Tang and Nilsson [9] on two different cement-based mixtures after a 24 h migration test.

Table 4 - Pore solution extraction and porosity measurement. The extracted concentration showed are adjusted to respect the electroneutrality requirement.	
Ions	Concentration (mmol/L)
OH$^-$	515.6
Na$^+$	176.6
K$^+$	354.8
SO$_4^{2-}$	9.0
Ca^{2+}	1.1
Porosity	0.184

approximately 120 h. Electrical current measurements are easier to perform and less labor intensive than the determination of chloride profiles usually performed for non steady-state migration experiments. Current measurements are also inherently more precise due to modern instrumentation.

5.2 Description of the calculation method

The current values are analyzed with the coupled extended Nernst-Planck-Poisson set of equations, *i.e.* Equations (14) and (15):

$$\frac{\partial C_i}{\partial t} - \frac{\partial}{\partial x}\left(D_i \frac{\partial C_i}{\partial x} + \frac{D_i z_i F}{RT} C_i \frac{\partial \Psi}{\partial x} + D_i C_i \frac{\partial \ln \gamma_i}{\partial x}\right) = 0$$

$$\tau \frac{d^2 \Psi}{dx^2} + \frac{F}{\varepsilon} \sum_{i=1}^{N} z_i C_i = 0$$

The boundary conditions correspond to the concentrations in both cells as well as the imposed potential difference across the sample. The short duration of the experiment, and the corresponding small total flux of species, allows for the assumption that concentrations in both the upstream and downstream reservoirs remain constant. As suggested earlier, the chemical reactions are neglected.

The initial conditions are determined by the pore solution chemistry and the porosity of the sample prior to the test. The total pore volume of the material can easily be determined according to ASTM C 642. Information on the chemical make-up of the pore fluid can be obtained by performing a pore solution extraction experiment according to the procedure described by Barneyback and Diamond (see reference [46]). A special extraction cell specifically designed to accommodate concrete samples is used. Solution samples collected during the tests are analyzed by ion chromatography.

With these data, the equations are solved with different tortuosity values. The numerical current I_c^{num} is calculated at the measurement times according to [16]:

$$I_c^{num} = SF \sum_{i=1}^{N} z_i J_i \qquad (20)$$

where S is the exposed surface area of the sample and J_i is the ionic flux given by Equation (13):

$$J_i = -\phi D_i \frac{\partial C_i}{\partial x} - \phi \frac{D_i z_i F}{RT} C_i \frac{\partial \Psi}{\partial x} - \phi D_i C_i \frac{\partial \ln \gamma_i}{\partial x}$$

For each tortuosity value, the error between the model and the measurements is calculated as:

$$error = \sqrt{\sum_{k=1}^{M} \left(I_{c,k}^{mes} - I_{c,k}^{num}\right)^2} \qquad (21)$$

where M is the total number of measurements, and I_c^{mes} and I_c^{num} are the measured and predicted currents, respectively. The tortuosity value leading to the smallest error with the measurements yields the best estimate of the diffusion coefficient for each ionic species in the material considered. This analysis procedure is automated in a numerical code which yields the diffusion coefficients of OH$^-$, Na$^+$, K$^+$, SO$_4^{2-}$, Ca^{2+} and Cl$^-$ that minimize the error with the measured currents.

Table 5 - Results of the migration test. V_s stands for the potential difference at the sample's boundaries. The uncertainty attributed to V_s corresponds to the standard deviation of the set of measurements performed during a test.				
Conditions	Disks	V_s (V)	Tortuosity (1)	DCl (10^{-11} m^2/s)
0.5M NaCl 12 V	1	10.3±0.2	0.0303	6.17
	2	10.3±0.2	0.0283	5.74
0.5M NaCl 6 V	1	5.1±0.1	0.0245	4.97
	2	5.2±0.1	0.0273	5.55
0.1M NaCl 12 V	1	10.6±0.1	0.0233	4.74
	2	10.4±0.2	0.0248	5.05
0.2M Na$_2$SO$_4$ 12 V	1	10.6±0.1	0.0214	
	2	10.9±0.1	0.0197	
Average:			0.0250	
Standard deviation:			0.0036	

5.3 Experimental validation of the method

For the purpose of this study, the method was tested on a series of mortar samples. The mortar mixture was prepared at a water/cement ratio of 0.5 with a CSA Type 10 cement and a standard (ASTM C109 Ottawa) sand. The volume proportion of the sand was 50%. The specimens were cast in 100 mm diameter, 200 mm long cylindrical molds under vacuum to avoid air-void formation. The day after casting, the samples were demoulded and sealed in aluminum foil for 18 months. After the curing period, the foil was removed and the cylinders were sawn into 25 mm thick disks. The samples to be tested were saturated in a 300 mmol/L NaOH solution for 24 h. An additional disk was saturated in the same conditions. It was then subjected to a pore pressing experiment in order to measure the ionic content of the pore solution. Finally, another sample was used to determine the porosity of the material. The porosity and pore solution measurements are given in Table 4. The measured concentrations were adjusted to respect the electroneutrality requirement. Otherwise, problems with the numerical model could occur.

The samples were then tested according to the non steady-state migration procedure described in the previous section. In order to validate the approach, the samples were subjected to different test conditions, which are summarized in Table 5. For each test condition, two disks
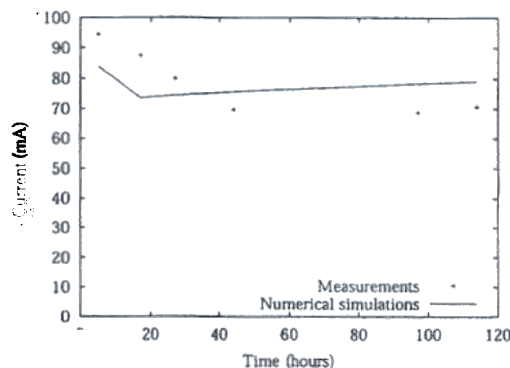
Fig. 6 - Comparison of the measured current with the numerical model for the case with 500 mmol/L NaCl in the upstream cell, 12 V applied, disk 1.

were tested. The potentials cited in Table 5 are those applied to the whole migration cell (see Fig. 1). During the experiment, a small drop of potential typically occurs in both compartments. So throughout the test, the potential difference across the sample V_s was measured regularly. The error estimation corresponds to the standard deviation over all the potential measurements made during a test. The small value of this error indicates stable conditions throughout the experiment. The value of V_s corresponds to the boundary condition of the potential at $x=L$ in the numerical code. The tests lasted 114 h for the first four samples and 121 h for the remaining ones. Six current measurements are made during the tests.

The numerical model is then used to analyze the measured currents. The tortuosity and chloride diffusion coefficient found for each disk tested are given in Table 5. Even if the method gives the diffusion coefficient for all species present in the system, only the value for chloride is given. Equation (3), in combination with the diffusion coefficient in free water, must be used in order to have the diffusion coefficient values for the other species. The results listed in Table 5 have an average value of $(5.07\pm0.72) \times 10^{-11}$ m^2/s. The error value corresponds to the standard deviation. A typical current curve, showing the comparison between the measurements and the numerical results, is shown in Fig. 6.

5.4 Discussion

The proposed method avoids the applied electrical potential dependency exhibited by other analysis procedures found in the literature. The constant field assumption, which neglects the internal coupling among the ions during a migration test, was identified as a possible cause for this behavior. The results for the 500 mmol/L NaCl in the upstream cell with 12 V and 6 V (see Table 5, the four first rows), show only a slight dependency upon the applied potential. The average value of the chloride diffusion coefficient for the four disks is $(5.61\pm0.50) \times 10^{-11}$ m^2/s, the uncertainty (standard deviation) being smaller than the uncertainty for the whole set of experiments (±0.72).

The migration tests performed with 100 mmol/L NaCl and 200 mmol/L Na$_2$SO$_4$ gave results that, although in the

same range of values as the other results, are smaller. This tends to show an effect of the concentration level and/or the migrating salt in the upstream cell on the diffusion coefficient. Since it was shown in Fig. 4 that the chemical activity gradient has virtually no effect on the concentration profile, these variations related to the concentration could come from the neglected chemical reactions.

It is interesting to note that the current drop measured at the beginning of the test is also predicted by the model (see Fig. 6). Upon closer examination, this behavior is to be expected. To transport chloride and sulfate ions out of the upstream reservoir, the electric field points from the downstream to the upstream reservoir. At the upstream interface, the chloride concentration in the sample is increasing, but the hydroxyl concentration is decreasing faster because the hydroxyl ions are more mobile. At the downstream interface, 0.3 mol/L sodium ions are replacing 0.18 mol/L sodium and 0.35 mol/L potassium ions. Moreover, because the potassium ion has a greater mobility than sodium, the downstream interface is becoming depleted of cations. As a net result, the ionic strength at both ends of the sample decrease, decreasing the overall conductivity, leading to a reduction in the current. For one-dimensional transport, even a thin layer of low conductivity material can have a dramatic effect on the overall bulk conductivity.

6. CONCLUSION

This study demonstrated that the commonly used constant field hypothesis should not be used to model the migration experiment. Instead, a multiionic model considering the electrical coupling among the ions should be applied.

The proposed approach is based on a non-steady-state analysis of the migration test with the extended Nernst-Planck/Poisson set of equations. The chemical reactions are neglected from the analysis. Although the complete method requires a more sophisticated calculation than that typically employed, it also offers some advantages: It is based on current measurements that are less expensive and easier to perform than the chloride concentration evaluations that are frequently used with the migration test. The method gives the diffusion coefficient of each ionic species in the material, according to the theory of homogenisation used to develop the mathematical model. The tests have shown that it is not dependent on the external potential applied to the sample. Finally, it is slightly dependent on the concentration level in the upstream cell as well as on the type of electrolyte in this cell.

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