

Dimensional analysis of ionic transport problems in hydrated cement systems. Part 1. Theoretical considerations

by

R. Barbarulo ^{a,b}, J. Marchand ^a

**^a CRIB, Département de génie civil
Université Laval
Sainte-Foy, Quebec, Canada, K1K 7P4**

and

K.A. Snyder

**Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899 USA**

and

S. Prené ^b

**^b Division Recherche et Développement
Département EME, Electricité de France
77250 Moret-sur-Loing, France**

Reprinted from the *Cement and Concrete Research*, Vol. 30, No.12, 1955-1960, December 2000.

NOTE: This paper is a contribution of the National Institute of Standards and Technology and is not subject to copyright.



NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce



Dimensional analysis of ionic transport problems in hydrated cement systems

Part 1. Theoretical considerations

R. Barbarulo^{a,b}, J. Marchand^{a,*}, K.A. Snyder^c, S. Prené^b

^aCRIB, Département de génie civil, Université Laval, Sainte-Foy, Québec, Canada, G1K 7P4

^bDivision Recherche et Développement, Département EMA, Electricité de France, 77250 Moret-sur-Loing, France

^cBFRL, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

Received 24 January 2000; accepted 31 July 2000

Abstract

The validity of the local equilibrium assumption in hydrated cement systems that a particular chemical reaction is instantaneous with respect to transport is examined using a dimensional analysis of electrochemical transport in cementitious materials. The transport equation parameters are scaled, resulting in a dimensionless equation. The dimensionless coefficient for each reaction/transport term determines its relative contribution to the overall process. The diffusion of ions in a reactive porous medium can be fully described on the basis of six independent dimensionless numbers. The analysis demonstrates that the kinetics of the reaction determine the appropriate time constant for the analysis. The formalism is applied to the dissolution of calcium hydroxide under an electrochemical potential gradient. The results are in agreement with previous observations and demonstrate quantitatively the local equilibrium hypothesis is valid in most practical cases where ions are transported by diffusion through a saturated material. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Transport properties; Modeling; Cement systems; Reaction

1. Introduction

The transport and reaction of ionic species within concrete are not only important in the critical role they play in the development of deleterious chemical reactions. They also affect the transport of ions through changes in the material pore structure. In that respect, the dissolution/precipitation of solid phases has been found to have a significant influence on the durability of construction materials. For instance, the dissolution of calcium carbonate is one of the main parameters that controls the service life of sandstone used for architectural applications [1]. The formation of new sulfate or chloride bearing phases is also known to have detrimental effects on the behavior of cement systems such as concrete and mortar [2–4].

In most models developed to predict the service life of construction materials, the influence of on-going chemical reactions on the mechanisms of transport is usually taken into account by simply assuming the existence of a local chemical equilibrium [5]. According to this hypothesis, the rate of dissolution/precipitation of the various species in solution is intrinsically much faster than the rate of transport. The validity of this assumption rests on the observations that, in most degradation cases involving construction materials, chemical reactions usually progress as fronts originating from the external surfaces of the solid [6,7].

This aspect of the problem has, however, been the subject of very few systematic investigations. Furthermore, recent data tend to indicate that the local equilibrium assumption may not be valid in cases where ions are being transported very quickly through the material pore structure [8]. These cases include the transport of ions under an externally applied electrical potential.

* Corresponding author. Tel.: +1-418-656-2079; fax: +1-418-656-3355.

E-mail address: jmarchan@ci.ulaval.ca (J. Marchand).

The formalism demonstrated here reduces the governing transport equation to a dimensionless equation through the use of scaling variables. The original equation is transformed into one that contains a dimensionless coefficient for each term in the transport equation. The magnitude of the coefficient determines the relative contribution by that term to the overall transport.

While this technique has been used extensively in other fields of science and engineering, it is an underutilized tool in the field of concrete materials research. The basic features of the technique are presented in the following paragraphs. In Part 2 of this series, this theoretical framework will be applied to research on the electrochemical migration of calcium, hydroxide and chloride ions in cement pastes, and then applied in Part 3 to ionic transport in unsaturated materials.

2. Coupling transport and chemical reactions in cement-based materials

Consider a fluid-saturated porous material with porosity Φ , composed of an insoluble backbone with a single soluble phase ϕ . This soluble phase is composed of species χ_a and χ_b in the stoichiometric proportions ν_a and ν_b . The liquid phase in the material pore space contains the cation χ_a and anion χ_b in the respective concentrations c_a and c_b . The chemical equilibrium between the solid phase ϕ , and the pore solution can be described by the following congruent dissolution/precipitation equation:

$$\chi_a^{\nu_a} \chi_b^{\nu_b} = \nu_a \chi_a + \nu_b \chi_b \quad (1)$$

A diffusive transport equation for the solute species χ_a and χ_b is needed that can incorporate the reaction described in Eq. (1). The condition for chemical equilibrium between the solute species and the solid can be expressed in terms of the concentration of each species in solution:

$$(\gamma_a c_a)^{\nu_a} (\gamma_b c_b)^{\nu_b} = K_\phi^{\text{sp}} \quad (2)$$

where K_ϕ^{sp} is the equilibrium solubility constant of phase ϕ and γ_i is the associated chemical activity coefficient of the dissolved species χ_i .

According to Eqs. (1) and (2), congruent dissolution/precipitation reactions can occur in the system to restore the chemical equilibrium. For instance, ions can precipitate to form more solid phase ϕ . Conversely, when the solid phase ϕ is dissolved, its components χ_a and χ_b are released into the solution.

The dissolution/precipitation reactions are generally induced by the transport of ions within the material pore structure. In a fluid-saturated medium, the diffusion of an ionic species in the liquid phase can be described by the extended Nernst–Planck equation [5,9]. This equation, homogenized over a representative elementary volume of

the material [9], and including a term for chemical reactions, is given by the following:

$$\frac{\partial c_i}{\partial t} = \nabla D_i \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{z_i F}{RT} c_i \nabla \Psi_D \right) - \left(\frac{1 - \Phi}{\Phi} \frac{\partial c_i^{(s)}}{\partial t} \right)_\phi \quad (3)$$

Ionic transport
Chemical reaction

The quantity c_i is the concentration of ionic species χ_i in the liquid phase, z_i is its valence, D_i is the diffusion coefficient of this species in the porous environment, γ_i is the activity coefficient of the species, $c_i^{(s)}$ is the concentration of compound χ_i in the solid phase and Ψ_D is the diffusion potential.

In Eq. (3), the electric coupling is assured through the diffusion potential Ψ_D , which arises from differences among diffusion coefficients of the ionic species present [5,9,10]. The diffusion potential Ψ_D can be calculated according to the Poisson equation (averaged over the representative elementary volume):

$$\Gamma \nabla^2 \Psi_D + \frac{F}{\epsilon} \left(\sum_{i=1}^N z_i c_i \right) = 0 \quad (4)$$

where Γ is the tortuosity of the liquid phase, ϵ the dielectric constant of the medium and N the number of ionic species in solution. Eqs. (3) and (4) represent a complete electrochemical description of ionic diffusion transport in a reactive porous medium [4].

The term $((\partial c_i^{(s)})/(\partial t))_\phi$ in Eq. (3) quantifies the exchange between the solid phase and the liquid phase of a given ionic species. When local equilibrium between the solid phase and the surrounding solution is preserved, this term can be described either by reaction isotherms [4] or by calculating the solubility products of the solid phases present in the system [5,11].

Another more general way of describing the reaction is to assume that the rate of the dissolution/precipitation will increase proportionally as the system deviates from its equilibrium condition. The term $((\partial c_i^{(s)})/(\partial t))_\phi$ can thus be expressed as a function of the concentrations in the pore solution:

$$\frac{\partial c_i^{(s)}}{\partial t} = \nu_i \kappa_\phi \left(\frac{\Phi}{1 - \Phi} \right) (K_\phi^{\text{sp}} - (\gamma_a c_a)^{\nu_a} (\gamma_b c_b)^{\nu_b}) \quad (5)$$

$i = a \text{ or } b$

where κ_ϕ is the reaction rate coefficient of dissolution/precipitation of the phase ϕ . In order to simplify the problem, the order of the reaction is assumed to be 1. The reaction rate coefficient is a physical quantity that can be determined experimentally. The determination of κ_ϕ will be further discussed in the following section.

Substituting Eq. (5) into Eq. (3) yields the following:

$$\frac{\partial c_i}{\partial t} = \underbrace{\nabla D_i \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{z_i F}{RT} c_i \nabla \Psi_D \right)}_{\text{Ionic transport}} + \underbrace{v_i \kappa_\phi (K_\phi^{sp} - (\gamma_a c_a)^{v_a} (\gamma_b c_b)^{v_b})}_{\text{Chemical reaction}} \quad (6)$$

Any variation in the concentrations of the various ionic species within the reactive porous medium can be described on the basis of Eq. (6).

3. Dimensional analysis

The main advantage of using Eq. (6) is that it does not rely on the local equilibrium assumption. Furthermore, the kinetic nature of the chemical reaction is delineated by the last term of the right-hand side of the expression. The rate of reaction can therefore be compared to the rate of ionic transport. Such a comparison can be done using dimensional analysis. This method is briefly described in the following paragraphs.

3.1. Ideal solutions in non-reactive porous media

As previously emphasized, the dimensional analysis essentially consists of reducing the governing transport equation to a dimensionless equation through the use of scaling variables [12–15]. The approach can be divided in four different steps:

1. Identification of the characteristic values (scaling parameters) of the problem.
2. Identification of the dimensional quantities and fundamental units of the problem.
3. Reduction of the governing equations to a dimensionless expression.
4. Identification of the dimensionless numbers.

As an example of dimensional analysis, consider the dilute limit approximation for diffusive transport under an electrochemical potential. Given the ideality of the ionic solutions, activity effects can be neglected. Furthermore, let us assume that there is no chemical interaction of the solid phase and the ionic species in solution. The transport problem for N ions can therefore be described by the following equation:

$$\frac{\partial c_i}{\partial t} = \nabla D_i \left(\nabla c_i + \frac{z_i F}{RT} c_i \nabla \Psi_D \right) \quad i = 1, \dots, N \quad (7)$$

Eq. (7) can be normalized by using the following dimensionless variables:

$$\bar{c}_i = \frac{c_i}{c_0}, \quad \bar{x} = \frac{x}{L_0}, \quad \bar{t} = \frac{t}{\tau}, \quad \bar{\Psi} = \frac{\Psi_D}{\Psi_0} \quad (8)$$

The scaling parameters c_0 , L_0 , τ , and Ψ_0 are values characteristic of the problem being analyzed [15,16]. For instance, L_0 is the maximum length of the domain. Similarly, c_0 represents the maximum concentration that can be reached at any point in the system and the value of Ψ_0 corresponds to the largest drop in potential across the domain. The scaled variables range in value from 0 to 1.

By introducing these dimensionless variables, Eqs. (4) and (7) may be written in their dimensionless forms [Eqs. (9) and (10)]:

$$\Gamma \nabla^2 \bar{\Psi} + \frac{c_0 L_0^2 F}{\epsilon \Psi_0} \left(\sum_{i=1}^N z_i \bar{c}_i \right) = 0 \quad (9)$$

$$\frac{\partial \bar{c}_i}{\partial \bar{t}} = \frac{\tau D_i}{L_0^2} \nabla \left(\nabla \bar{c}_i + z_i \frac{F \Psi_0}{RT} \bar{c}_i \nabla \bar{\Psi} \right) \quad i = 1, \dots, N \quad (10)$$

According to Buckingham’s π theorem, if a system is described by n independent dimensional variables, and if m fundamental units are necessary to express these variables, all relations between the n variables can be expressed by using $(n - m)$ dimensionless numbers (or π ’s as they are called) [12–15]. The system defined by Eqs. (4) and (7) can be fully described by $n = 8 + N$ independent dimensional quantities (c_0 , L_0 , τ , Ψ_0 , D_i , T , F , R , ϵ) and $m = 6$ fundamental units (length (m), time (s), mass (kg), quantity of ions (mol), temperature ($^\circ\text{K}$), and current intensity (A)). Consequently, according to the theorem, the relation between the dimensional variables can be expressed by using $(8 + N - 6 = N + 2)$ dimensionless numbers [Eq. (11)]:

$$\left(\frac{\tau D_i}{L_0^2} \right), N - 1 \text{ numbers } \left(\frac{D_i}{D_j} \right), \left(\frac{c_0 L_0^2 F}{\epsilon \Gamma \Psi_0} \right), \text{ and } \left(\frac{F \Psi_0}{RT} \right) \quad (11)$$

As previously mentioned, the magnitude of a dimensionless number indicates its relative importance on the overall transport process. A large number (i.e. $\gg 1$) indicates that the phenomenon under consideration dominates the behavior of the system. Phenomena with little influence are characterized by small dimensionless numbers (i.e. $\ll 1$). A number on the order of 1 reveals that the system is affected but not dominated by the phenomenon.

The first dimensionless number $((\tau D_i)/(L_0^2))$ provides information on the characteristic time required by a given species to diffuse through the system. The numbers (D_i/D_j) compare the diffusion coefficient of one species to the other. The third dimensionless number $((c_0 L_0^2 F)/(\epsilon \Gamma \Psi_0))$ characterizes the linearity of the diffusion potential Ψ_D distribution across the system. Large values of $((c_0 L_0^2 F)/(\epsilon \Gamma \Psi_0))$ indicate that the distribution of the potential is essentially non-linear (i.e. the electric field is not constant).

From the standpoint of modeling, the last dimensionless number $((F\Psi_0)/(RT))$ is quite interesting since it provides information about the relative importance of the diffusion potential term on the overall transport process. Such a comparison is similar to the calculation of the Peclet number for any hydrodynamic problem [17].

Obviously, the value of $((F\Psi_0)/(RT))$ is directly affected by the characteristic potential drop Ψ_0 . Its value can be established on the basis of numerical simulations or by experimental measurements. For most practical problems, Ψ_0 is usually on the order of a few tens of millivolts [18,19]. This value is typical of hydrated cement systems for which the characteristic length L_0 is approximately a few centimeters (e.g. the thickness of a diffusion cell sample or the thickness of the cover of a reinforced concrete structure). Therefore, it can be easily calculated that, at 25°C, $((F\Psi_0)/(RT))$ is on the order of 1.

This result is particularly important since it clearly emphasizes the significant contribution of the diffusion potential to the overall transport process. It also justifies the use of the Nernst–Planck/Poisson set of equations to model ionic diffusion problems in hydrated cement systems and confirms the observation that ionic transport mechanisms cannot be simply modeled by Fick's equation (which neglects the effect of the diffusion potential) [18,20].

3.2. Concentrated electrolytes in reactive porous media

The equation used here for the rate of change in concentration for reacting concentrated electrolytes is similar to that of Eq. (6):

$$\frac{\partial c_i}{\partial t} = D_i \nabla \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{z_i F}{RT} c_i \nabla \Psi_D \right) + \nu_i \kappa_\phi \left(K_\phi^{\text{sp}} - (\gamma_a c_a)^{\nu_a} (\gamma_b c_b)^{\nu_b} \right) \quad (12)$$

Ionic transport
Chemical reaction

As can be seen, contrary to Eq. (6), Eq. (12) is written in such a way that the diffusion coefficients of the various species in solution are assumed to be unaffected by the chemical reaction, so that D_i can be taken outside the gradient operator in the ionic transport part of Eq. (12). This assumption simplifies the mathematical treatment of the problem. However, it should be emphasized that this is clearly an oversimplification of the problem since chemical reactions are known to modify the transport properties of hydrated cement systems [6,21,22].

This system defined by Eq. (12) can be fully described by $n = 10 + N$ dimensional quantities (c_0 , L_0 , τ , Ψ_0 , D_i , T , F , R , ϵ , K_ϕ^{sp} , and κ_ϕ) and $m = 6$ fundamental units (length (m), time (s), mass (kg), quantity of ions (mol), temperature (°K), and current intensity (A)). Accordingly, the relation between the dimensional variables can be expressed by using $(10 + N - 6 = 4 + N)$ dimensionless numbers.

Eq. (12) can be normalized using the same dimensionless variables as those described in Eq. (8):

$$\frac{\partial \bar{c}_i}{\partial \bar{t}} = \frac{\tau D_i}{L_0^2} \nabla \left(\nabla \bar{c}_i + z_i \frac{F \Psi_0}{RT} \bar{c}_i \nabla \bar{\Psi} \right) + \nu_i (\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1}) \times \left(\frac{K_\phi^{\text{sp}}}{c_0^{\nu_a + \nu_b}} - \bar{c}_a^{\nu_a} \bar{c}_b^{\nu_b} \right) \quad i = 1, \dots, N \quad (13)$$

As can be seen, the normalization of Eq. (13) creates two new dimensionless numbers [Eq. (14)]:

$$\left(\frac{K_\phi^{\text{sp}}}{c_0^{\nu_a + \nu_b}} \right) \text{ and } (\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1}) \quad (14)$$

The quantity $\left(\frac{K_\phi^{\text{sp}}}{c_0^{\nu_a + \nu_b}} \right)$ can be used to verify whether the system is anywhere close to its equilibrium condition. The number $(\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1})$ determines the scale of the kinetics of reaction. From the standpoint of modeling, this number is particularly important since it provides information on the relative influence of the reaction term on the global behavior of the system. For cases for which $(\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1})$ is far greater than $((\tau D_i)/(L_0^2))$, the reaction term will dominate any changes in concentration. It is on these scales that the local equilibrium is preserved and one may approximate the reaction as instantaneous with respect to the ionic transport process. In these instances, the ionic diffusion problem can be modeled using Eq. (3), which does not include any reaction rate coefficient κ_ϕ and in which instantaneous chemical reaction is implicit. This represents a significant practical advantage since values of κ_ϕ are usually cumbersome to obtain experimentally.

For cases in which $((\tau D_i)/(L_0^2))$ is far greater than $(\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1})$, the behavior of the system will be totally dominated by the transport process. In some cases, the contribution of the reaction term can even be neglected and the problem can be modeled by the following equation [Eq. (15)]:

$$\frac{\partial c_i}{\partial t} = D_i \nabla \left(\nabla c_i + c_i \nabla \ln \gamma_i + \frac{z_i F}{RT} c_i \nabla \Psi_D \right) \quad (15)$$

Finally, on scales for which $((\tau D_i)/(L_0^2))$ is on the order of $(\kappa_\phi \tau c_0^{\nu_a + \nu_b - 1})$, the behavior of the system will not be dominated by any of the various processes involved. In these cases, the problem has to be modeled by Eq. (6), which requires the determination of the rate coefficients for each chemical reaction involved in the system.

3.3. Numerical example: calcium hydroxide leaching

Calcium hydroxide is the most soluble phase produced by the hydration of cement with water. Its dissolution contributes to local increases in the porosity. From the standpoint of durability, the study of the calcium hydroxide dissolution mechanism is of interest. For this particular case, the phase ϕ previously defined thus corresponds to

$\text{Ca}(\text{OH})_2$, $\chi_a = \text{Ca}^{2+}$ and $\chi_b = \text{OH}^-$, $\nu_a = 1$ and $\nu_b = 2$. By solving Eq. (5) for the dissolution of calcium hydroxide, a relationship between t_{CH} (i.e. the time needed to reach a 99% saturation after the immersion of the dissolving solid pure water) and the kinetic constant κ_{CH} can be found [Eq. (16)]:

$$\kappa_{\text{CH}} = \frac{2.38}{4^{1/3} (K_{\text{CH}}^{\text{sp}})^{2/3}} \times \frac{1}{t_{\text{CH}}} \quad (16)$$

where t_{CH} is the characteristic time of calcium hydroxide dissolution in pure water. The equilibrium constant of $\text{Ca}(\text{OH})_2$ is $K_{\text{CH}}^{\text{sp}} = 10^{3.75} \text{ (mol/m}^3\text{)}^3$. The value of t_{CH} was estimated by conductimetry measurements to be approximately 6 min. Assuming a first-order reaction, this corresponds to a rate constant κ_{CH} of $1.3 \times 10^{-5} \text{ m}^6/\text{mol}^2 \text{ s}$.

Let us consider a concrete sample immersed in pure water. The pore solution of the material is initially in equilibrium with calcium hydroxide. The equilibrium constant of $\text{Ca}(\text{OH})_2$ is $K_{\text{CH}}^{\text{sp}} = 10^{3.75} \text{ (mol/m}^3\text{)}^3$, so that $c_0 = 18 \text{ mmol/l}$. The diffusion coefficients of the hydroxyl and calcium ions in the 0.45 water/cement ratio concrete mixture considered are $D_{\text{OH}} = 9.0 \times 10^{-12} \text{ m}^2/\text{s}$ and $D_{\text{Ca}} = 1.4 \times 10^{-12} \text{ m}^2/\text{s}$, respectively [4].

Diffusion and reaction rates are of the same magnitude when $((\tau D_i)/(L_0^2))$ is on the order of $(\kappa_{\phi} \tau c_0^{\nu_a + \nu_b - 1})$. This implies that [Eq. (17)]:

$$L_0 = \sqrt{\frac{D_i}{\kappa_{\phi} c_0^{\nu_a + \nu_b - 1}}} \text{ i.e. } L_0 \cong 46 \text{ } \mu\text{m} \quad (17)$$

Therefore, the distance at which one can neglect the finite time for calcium hydroxide dissolution is characterized by 46 μm . This value was obtained by considering that the overall process was dominated by the fastest ion (i.e. $D_i = D_{\text{OH}} = 9.0 \times 10^{-12} \text{ m}^2/\text{s}$). Beyond this distance, the reaction contribution increases proportionally to L_0^2 . At a distance of approximately 100 μm , the contribution from the reaction term is nearly 10 times greater than that of the diffusion term, and so dissolution could be considered instantaneous with respect to diffusion. These results are quite significant considering that the representative volume of most hydrated cement systems is on the order of a few cubic centimeters (or more) and that most practical problems involve concrete elements, which are at least a few centimeters thick.

Considering that the hydroxyl ion is one of the fastest diffusing species found in cement systems, the previous analysis can probably be directly applied to most practical cases involving the transport of ions in saturated concrete. Although the precipitation process of chloride and sulfate-bearing phases has been found to be somewhat slower than the dissolution of calcium hydroxide [23,24], the reduction in the kinetics of reaction is not sufficient to significantly modify the previous results. In that respect, the dimensional analysis clearly confirms the assumption that, in most

practical cases involving the diffusion of ions in saturated cement systems, the local equilibrium is preserved [6,7].

It should also be emphasized that the technique demonstrated here also has use in the analysis of experimental data. In both steady state and transient tests, researchers typically make the assumption that the reaction rate is relatively instantaneous by comparison to the other transport mechanism. In most cases, this is probably true. However, it is conceivable that this assumption may not apply to cases where ions are transported very quickly through the material pore structure, for example, by an applied electric field. This aspect of the problem will be further discussed in Parts 2 and 3 of the present series.

4. Conclusion

The analysis performed here demonstrates a useful technique for comparing the significance of different contributions to ionic transport, and the ensuing chemical degradations, in concrete. It has been shown that the diffusion of ions in a reacting porous medium can be fully described on the basis of six different dimensionless numbers. The analysis also demonstrates that the kinetics of the reaction determine the appropriate treatment of the overall transport problem.

The formalism is applied to dissolution of calcium hydroxide under an electrochemical potential gradient. The results are in agreement with previous observations and demonstrate quantitatively the local equilibrium hypothesis is valid in most practical cases where ions are transported by simple diffusion through a saturated material.

Acknowledgments

The authors are grateful to Electricité de France (Division Recherche et Développement, Département Etude des Matériaux), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Institute of Standards and Technology (NIST) for their financial support for this project. The authors would also like to thank Dr. E.J. Garboczi, Dr. N.S. Martys and Dr. J.J. Beaudoin for several useful discussions during the course of this research.

References

- [1] G.G. Amoroso, V. Fassina, Stone decay and conservation: Atmospheric pollution, cleaning, consolidation and protection, in: National Scientific Research Fund of Switzerland (Eds.), Materials Science Monographs, Vol. 11, Elsevier, The Netherlands, 1983, pp. 69–74.
- [2] D. Damidot, F.P. Glasser, Thermodynamic investigation of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{CaSO}_4-\text{H}_2\text{O}$ system at 25°C and the influence of Na_2O , *Concr Res* 23 (1) (1993) 221–238.
- [3] L.O. Nilsson, E. Poulsen, P. Sandberg, P. Sosenren, O. Klinghoffer, Chloride penetration into concrete, state of the art: Transport pro-

- cesses, corrosion initiation, test methods and predicting models, HE-TEK Report No 53, Road Directorate, Denmark, 1996.
- [4] J. Marchand, E. Samson, Y. Maltais, Modeling microstructural alterations of concrete subjected to external sulfate attack, in: J.P. Skalny, J. Marchand (Eds.), *Materials Science of Concrete — Sulfate Attack Mechanisms*, American Ceramic Society, Westerville, OH, 1999, pp. 211–258.
- [5] J. Marchand, B. Gérard, A. Delagrave, Ion transport mechanisms in cement-based materials, in: J.P. Skalny (Ed.), *Materials Science of Concrete*, Vol. 5, American Ceramic Society, Westerville, OH, 1998, pp. 307–400.
- [6] F. Adenot, *Concrete durability: Modeling the chemical and physical damage processes*, PhD Thesis, Université d'Orléans, France, 1992 (in French).
- [7] E. Revertégat, F. Adenot, C. Richet, L. Wu, F.P. Glasser, D. Damidot, S.A. Stronach, Theoretical and experimental study of degradation mechanisms of cement in the repository environment, Final Report (EUR 17642 EN), Nuclear Science and Technology, European Atomic Energy Community, 1997.
- [8] M. Castellote, C. Andrade, C. Alonso, Chloride-binding isotherms in concrete submitted to non-steady-state migration experiments, *Cem Concr Res* 29 (11) (1999) 1799–1806.
- [9] E. Samson, J. Marchand, J.J. Beaudoin, Describing ion diffusion in cement-based materials using the homogenization technique, *Cem Concr Res* 29 (8) (1999) 1341–1345.
- [10] F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, USA, 1961.
- [11] E. Samson, J. Marchand, J.J. Beaudoin, Modeling the influence of chemical reactions on the mechanisms of ionic transport in porous materials: An overview, *Cem Conc Res* 30 (12) (2000) 1895–1902.
- [12] A.A. Gukhman, *Introduction to the Theory of Similarity*, Academic Press, New York, USA, 1965, pp. 234–238.
- [13] H.L. Langhaar, *Dimensional Analysis and Theory of Models*, Wiley, New York, USA, 1951.
- [14] G. Murphy, *Similitude in Engineering*, Ronald Press, New York, USA, 1950, pp. 36–40.
- [15] W.F. Hughes, J.A. Brighton, *Fluid Dynamics*, Schaum's Outline Series in Engineering, McGraw-Hill, New York, USA, 1967, pp. 62–74.
- [16] J. Bear, Y. Bachmat, *Introduction to Modeling of Transport Phenomena in Porous Media*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1991, pp. 271–274.
- [17] F.A.L. Dullien, *Porous Media: Fluid Transport and Pore Structure*, 2nd edn., Academic Press, New York, USA, 1991, pp. 489–526.
- [18] J. Marchand, T. Zhang, E. Samson, J.J. Beaudoin, J. Duchesne, Ionic diffusion mechanisms in porous media: Part 2. Experimental validation, 2000, submitted for publication.
- [19] J.Z. Zhang, N.R. Buenfeld, Presence and possible implications of the membrane potential in concrete exposed to chloride solutions, *Cem Concr Res* 27 (6) (1997) 853–860.
- [20] L. Tang, Concentration dependence of diffusion and migration of chloride ions — Parts 1 and 2, *Cem Concr Res* 29 (9) (1999) 1463–1474.
- [21] D.P. Bentz, E.J. Garboczi, Modeling the leaching of calcium hydroxide from cement paste: Effects on pore space percolation and diffusivity, *Mater Struct* 25 (1992) 523–533.
- [22] A. Delagrave, B. Gérard, J. Marchand, Modeling calcium leaching mechanisms in hydrated cement pastes, in: *Mechanisms of Chemical Degradation of Cement-Based Systems*, E&FN Spon, London, UK, 1992, pp. 38–47.
- [23] A. Atkinson, J. Hearne, Mechanistic model for the durability of concrete barriers exposed to sulphate-bearing groundwaters, *MRS Proceedings*, Vol. 176, Materials Research Society, Pittsburgh, PA, 1990, pp. 149–156.
- [24] L. Tang, L.O. Nilsson, Chloride binding capacity and binding isotherms of OPC pastes and mortars, *Cem Concr Res* 23 (3) (1993) 247–253.