ELSEVIER

Nonlinear Transient Phenomena in Porous Media with Special Regard to Concrete and Durability

B.F. Johannesson
Division of Building Materials, Lund Institute of Technology, Lund, Sweden

Concrete deteriorates due to many different mechanisms. Among the most important mechanisms is the reinforcement corrosion induced by deleterious substances reaching the embedded reinforcement bars. The external sources of deleterious materials may, for example, be deicing salts, sea water, and carbon dioxide. Research has sought to determine threshold values, in terms of concentration of deleterious substances in concrete, at which reinforcement corrosion will be induced, that is, at which concentration the passive condition close to the reinforcement turns to an aggressive state. To predict when this threshold value is reached, the flow properties of the pollutant in concrete must be known. Some of the most important phenomena governing the movement of pollutants in concrete are diffusion of substances in the pore water, adsorption (and desorption) of pollutants onto the pore walls, and hydrodynamic dispersion and convection of substances due to flow of the pore water. Here a set of equations will be presented based on mass and energy balance. These coupled equations cope with the above-mentioned phenomena. The migration of ions due to an electric potential is not considered as only the initiation stage of corrosion is of interest. The constituents considered in the model are a solute γ (e.g., chlorides), the pore water α, and the solid phase s of the concrete, which is restricted to be nondeformable. The governed equation system is solved using the Petrov-Galerkin scheme and finite elements (compare references 1 and 2). Some examples of the performance of the proposed model are given. ADVANCED CEMENT BASED MATERIALS 1997, 6, 71–75.

KEY WORDS: Concrete, Chloride diffusion, Chloride binding, Convection, Finite Elements, Petrov-Galerkin scheme

Corrosion of steel in concrete occurs whenever external influences change the composition of the pore solution, present in the concrete, to an aggressive condition. For example, chloride ions present in the pore solution and carbonation of the concrete may destroy the passivity of the steel, which results in corrosion of the reinforcement [3]. For this reason, one is interested in predicting the magnitude of mass transfer (e.g., diffusion) of deleterious substances, e.g., NaCl, from external sources into concrete. External influences such as capillary suction of water will also contribute to flows of deleterious substances carried by the water phase (convection). This phenomenon is perhaps the most important cause of penetration of pollutants in concrete structures exposed to moisture uptake and drying (compare reference 4).

The problem of penetration of dissolved matter into concrete will be solved as an *ideal tracer* problem that, for example, has been used to describe spreading of pollutants in groundwater [5]. The ideal tracer condition is defined as one that is inert with respect to its liquid and solid surroundings and that does not affect the liquid's properties. At relatively low concentrations of pollutants in the pore water, the ideal tracer approximation is sufficient for most practical purposes [5]. The ideal tracer problem is derived using the equations describing mass balance (i.e., charge balance is not considered) for the different constituents together with constitutive relations (compare references 5 and 6). To evaluate the Soret effect on the flow properties of the pollutant, a simple version of the energy equation for the whole mixture is also incorporated in the governing equation system.

The proposed model for flows of pollutants in concrete includes four state variables, that is, the volume fraction of pore water in the system $\theta_\alpha(x, t)$, the mass concentration of the pollutant in the pore water $C(x, t)$, the mass concentration of adsorbed substance (pollutant) in the solid $F(x, t)$, and the temperature of the whole mixture $T(x, t)$; the state variables are functions of position x and time t. Furthermore, the model contains only four material parameters in the isothermal case: the diffusion parameter for the pollute D_h, two material parameters describing adsorption, k, and desorption, m, of the pollutant, and one material parameter describing the mass transfer of pore water D_α. The diffusion properties of chlorides in different types of concrete have been experimentally verified [7], and the adsorption of chlorides onto the pore walls has been studied [3,7]. The parameters describing the mass transfer of pore water D_α have

---

Address correspondence to: B.F. Johannesson, Division of Building Materials, Lund Institute of Technology, Box 118, S-221 00, Lund, Sweden.
Received December 11, 1996; Accepted April 29, 1997

655 Avenue of the Americas, New York, NY 10010

ISSN 1065-7355/97/$17.00
PII S1065-7355(97)00013-8

been verified for concrete under isothermal drying conditions [8]. However, if the temperature T is included in the model, at minimum two additional material parameters must be introduced, i.e., the specific heat of the mixture $\tilde{C}_{tot}$, and the thermal conductivity of the mixture D_λ, which are well-known quantities.

The mass transfer of ions induced by an electrical potential between anodic and cathodic areas is not studied, as only the initiation stage of corrosion is of interest in this work. The propagation stage of corrosion has been dealt with [9].

The simulations performed with the proposed hypothetical model show that the convective part of the flow of deleterious matter plays a very important role when considering cases where the outer climate of pollutants and moisture is changed in time, as in the case of deicing salt exposure or at the "splash-zone" on a bridge column; this observation is in good agreement with field measurements on such constructions [3].

It is concluded that a model based on physical phenomena, capable of describing the coupling effects between the different constituents, is required to predict when the threshold values are reached close to the reinforcement. The following presentation is a step in this direction.

Convection—Diffusion Problems; Mass Balance

The mass balance for a solute γ (e.g., chlorides) in the α phase (e.g., pore water) is given [5], as:

$$\frac{\partial \theta_\alpha \bar{c}_\alpha}{\partial t} = -div[\bar{c}_\alpha q_\alpha + \theta_\alpha \overline{c_\alpha V_\alpha} + \theta_\alpha \overline{J(c_\alpha/\rho_\alpha)}] - f \quad (1)$$

where $\bar{c}_\alpha$ is the (averaged) mass of the pollutant γ per unit volume of α phase. θ_α is the volumetric fraction of α in the porous material. To obtain the *macroscopic* balance eq 1, the equation describing the *microscopic* balance [10] must be averaged. The averaging process performed to reach eq 1 results in two additional terms, compared with the microscopic balance equation [5]; first, $\theta_\alpha \overline{c_\alpha V_\alpha}$, which is the term describing the macroscopic *dispersive* flux of γ carried by the fluctuating velocity. The phenomenon on the macroscopic scale represents the loss of information by the passage from one scale of description to another, larger, one [5]. The second additional term, due to averaging, is the f term, which describes the transfer of γ across the boundaries of the α phase, e.g., *adsorption* or *desorption* of the pollutant γ. The first term in the bracket of eq 1 is the *convective* part of the flux, where the *specific discharge* $q_\alpha = \theta_\alpha \bar{u}_\alpha$ and $\bar{u}_\alpha$ is the *mean velocity of the mixture* (in this case the mean velocity of α). The third term in the bracket of eq 1 describes the flux of molecular diffusion of γ in the α phase.

The mass balance equation for the α phase (pore water), without source or sink terms, becomes:

$$\frac{\partial \theta_\alpha \bar{\rho}_\alpha}{\partial t} + div(\theta_\alpha \bar{\rho}_\alpha \bar{u}_\alpha) = 0 \quad (2)$$

where $\bar{\rho}_\alpha$ is the averaged mass density of the α phase. If the α phase is assumed to be incompressible (i.e., $div\bar{u}_\alpha = 0$) and assuming also small changes in $\bar{\rho}_\alpha$ due to the dissolved pollutant γ present in the α phase, i.e., $\bar{\rho}_\alpha =$ *const.*, eq 2 becomes:

$$\frac{\partial \theta_\alpha}{\partial t} + div(\theta_\alpha \bar{u}_\alpha) = 0. \quad (3)$$

The problem now reduces to an *ideal tracer problem*, or alternatively a *forced convection problem*, i.e., the mean velocity field $\bar{u}_\alpha$ is known (from eq 3) before eq 1 is solved.

When considering a porous medium that is deformable, the porosity will not be constant, i.e., θ_α will be affected; furthermore, the specific discharge vector q_α is defined with respect to the (possibly moving) solid parts of the porous medium. However, in this article it is assumed that the mean velocity of the solid phase is zero ($\bar{u}_s = 0$) i.e., no *consolidation* or *deformation* in the solid phase is dealt with.

Energy Conservation

The first axiom of thermodynamics involves two statements: one for the individual constituents (in this case the γ, α, and s phase) and one for the whole mixture [6]. The energy balance for the constituents involves constitutive-dependent terms describing the energy exchange between the phases that may be of importance. However, simplifying the problem using only a single temperature of the mixture, the local form of balance of energy becomes:

$$\rho\dot{\epsilon} = tr\mathrm{TL} - div\mathrm{h} + \rho r \quad (4)$$

where ρ is the density for the mixture, $\dot{\epsilon}$ is the material derivative of the *internal energy density* ϵ, and T and L are the *stress tensor* and *velocity gradient*, respectively. The heat flux vector is denoted by h, and r is the *external heat supply density*. As the momentum balance equation is not involved in the model, one is forced to ignore the first term on the right-hand side of eq 4; further, it is assumed that no external heat supply exist in the system, i.e., $r = 0$.

With the above-mentioned assumptions one will obtain the following simplified form of energy balance for the whole system:

$$\rho\dot{\epsilon} = div\mathrm{h}. \quad (5)$$

Constitutive Equations

The macroscopic flux, $\overline{J(c_\alpha/\rho_\alpha)}$, due to molecular diffusion of γ in the α phase, is expressed by:

$$J(c_\alpha/\rho_\alpha) = -D_{\gamma diff}\cdot grad\bar{c}_\alpha - D_{\gamma s}\cdot gradT \tag{6}$$

where $D_{\gamma diff}$ is the *second rank constitutive matrix*, which in many applications is assumed to be a function of $\bar{c}_\alpha$. Of course, molecular diffusion takes place even if the bulk mean velocity is zero, i.e., if $\bar{u}_\alpha = 0$. The second term on the right-hand side of eq 6 describes the Soret effect, and $D_{\gamma s}$ is the constitutive matrix that accounts for flow of γ in the α phase induced by a temperature gradient, which reproduces the well-known result that the gradient of the *chemical potential* provides the generalized force for flow of matter, i.e., matter tends to flow from regions of high chemical potential to regions of low chemical potential.

The molecular diffusion, adsorption and desorption of γ, i.e., chloride ions, must be electrically balanced by mass flow, and adsorption and desorption of other ions that do not directly contribute to corrosion, perhaps calcium and magnesium ions [9]. This fact may be used as an extra postulate when dealing with models with more than one electrically charged constituent.

The dispersive flux (not to be confused with the convective flux) induced by the spreading of γ in the α phase due to velocity variations at the microscopic level is, however, dependent on the bulk flow, molecular diffusion and the porous matrix geometry. It has been proposed [5] to use a Fickian type of law to describe the dispersive flux, such as:

$$\overline{c_\alpha V_\alpha} = -D_{\gamma disp}\cdot grad\bar{c}_\alpha \tag{7}$$

and to let the constitutive matrix $D_{\gamma disp}$ be a function of the bulk mean velocity $\bar{u}_\alpha$ and the Peclet number ($Pe = l\bar{u}_\alpha/D_{\gamma diff}$), where l is some characteristic length of the pores. For more details concerning the constitutive relation (eq 7), see reference 5.

The macroscopic flux, $\theta_\alpha\bar{u}_\alpha$, due to *capillary suction* and *moisture diffusion* of the α phase, is expressed as

$$\theta_\alpha\bar{u}_\alpha = -D_\alpha(\theta_\alpha)\cdot grad\theta_\alpha \tag{8}$$

where D_α is a function of θ_α.

The adsorption and desorption of the tracer γ across the α phase boundaries is constituted with a *nonequilibrium isotherm,* which describes a *reversible system* [11], as:

$$f \equiv \frac{\partial F}{\partial t} = k(C - mF); f_s = -f \tag{9a–b}$$

where $C = \bar{c}_\alpha/\bar{\rho}_\alpha$ = mass of γ per unit mass of α phase, and k and m are material parameters that may be functions of the temperature T. $F = \bar{c}_s/\bar{\rho}_s$ is the mass of γ per unit mass of solid. The right-hand side of eq 9a expresses the rate of transfer, f_s, of γ from the liquid phase α onto the solid phase s. Note that the behavior of both adsorption and desorption of chlorides is incorporated in the function f.

One may expect that existence of the mass source term f is due to free chloride ions reacting with calcium hydroxide at the solid pore walls. It is shown [12] that the binding capacity of chlorides is strongly dependent on the hydroxide ion concentration in the pore solution. This phenomenon is probably due to hydroxide ions and chloride ions competing for free sites at the solid pore walls. However, experiments also show that the desorption of chlorides is important, i.e., the chloride binding is reversible to some extent [3]. This type of behavior may be a consequence of a physical binding (rather than a chemical binding) and also a diffusion of chlorides into confined pores. A stringent physical description of the adsorption and desorption is important when considering variations in the chloride ion concentrations and relative humidities at the surface. It should be observed that the equation describing the adsorption and desorption of chlorides (eq 9) reduces to the so-called binding isotherm by setting $k(C - mF) = 0$. The use of this type of description is, however, not sufficient when considering arbitrary variation of the boundary conditions.

The simplified version of the energy equation 5 is rewritten using the internal energy density for the mixture ϵ, as:

$$\rho\left(\frac{\partial\epsilon}{\partial t} + \bar{u}_\alpha\cdot grad\epsilon\right) = div\mathrm{h}. \tag{10}$$

The internal energy density is approximated using the relation:

$$\epsilon = \tilde{C}_{tot}T, \tag{11a}$$

where

$$\tilde{C}_{tot} = \theta_s\tilde{C}_s + \theta_\alpha\tilde{C}_\alpha. \tag{11b}$$

The material parameter C_{tot} represents the volume fraction-weighted average of the specific heat of the mixture. The heat flux is described using the classical assumption (Fourier's law):

$$\mathrm{h} = D_\lambda\cdot gradT \tag{12a}$$

where

$$\lambda_{xx}^n = \lambda_{yy}^n = \lambda_{zz}^n = \theta_s\tilde{\lambda}_s^n + \theta_\alpha\tilde{\lambda}_\alpha^n \tag{12b}$$

where the conductivities λ_{xx}, λ_{yy}, and λ_{zz} are the only nonnegative quantities in the diagonal constitutive matrix D_λ. The conductivities are weighted using the volume fractions together with the exponent n, which is a number between −1 and 1. Equation 10 together with the constitutive relations (eqs 11a and 12a) takes the form:

$$\rho\tilde{C}_{tot}\left(\frac{\partial T}{\partial t}+\frac{1}{\theta_\alpha}\mathrm{q}_\alpha\cdot gradT\right)=div[\mathrm{D}_\lambda\cdot gradT]. \qquad (13)$$

Introducing the constitutive relations (eqs 6–7,9) into eq 1, and assuming that the mass change of the solid phase s due to adsorption and desorption of the tracer γ is small, i.e., $\bar{\rho}_s = const.$, $\theta_s = const.$, one will obtain:

$$\bar{\rho}_\alpha\frac{\partial\theta_\alpha C}{\partial t}+\bar{\rho}_s\theta_s k(C-mF)=$$

$$-div[\bar{\rho}_\alpha C\mathrm{q}_\alpha-\bar{\rho}_\alpha\theta_\alpha\mathrm{D}_h\cdot gradC-\mathrm{D}_{\gamma s}\cdot gradT] \qquad (14)$$

where $\mathrm{D}_h = \mathrm{D}_{\gamma diff} + \mathrm{D}_{\gamma disp}$ is the matrix describing *hydrodynamic dispersion*.

By combining eqs 3 and 14 and using the identity $div(C\mathrm{q}_\alpha) = Cdiv\mathrm{q}_\alpha + \mathrm{q}_\alpha\cdot gradC$, eq 14 may be written as:

$$\theta_\alpha\frac{\partial C}{\partial t}+\tilde{k}(C-mF)=div[\theta_\alpha\mathrm{D}_h\cdot gradC]$$

$$-\mathrm{q}_\alpha\cdot gradC+div[\theta_\alpha\mathrm{D}_{\gamma s}\cdot gradT] \qquad (15)$$

which is the convective-diffusion equation with two additional terms, describing a nonequilibrium reversible reaction and the Soret effect.

The equation for the α phase is given by eqs 3 and 8 as:

$$\frac{\partial\theta_\alpha}{\partial t}-div[\mathrm{D}_\alpha(\theta_\alpha)\cdot grad\theta_\alpha]=0; \qquad (16a)$$

and

$$\mathrm{q}_\alpha=-\mathrm{D}_\alpha(\theta_\alpha)\cdot grad\theta_\alpha. \qquad (16b)$$

The specific discharge, $\mathrm{q}_\alpha = \theta_\alpha\bar{u}_\alpha$, for the α phase is calculated with eq 16a–b; the result is used to express q_α in eqs 15 and 13. The model contains four state variables: θ_α given by eq 16a, C given by eq 15, and F given by eq 9a; the temperature T for the whole mixture is calculated using eq 13.

Results

Two different one-dimensional examples, case 1 and case 2, have been solved with the Petrov-Galerkin method [2] using finite elements. Both examples are calculated with the coupled eqs 16a, 16b, 15, and 9, with identical material parameters for the two cases.

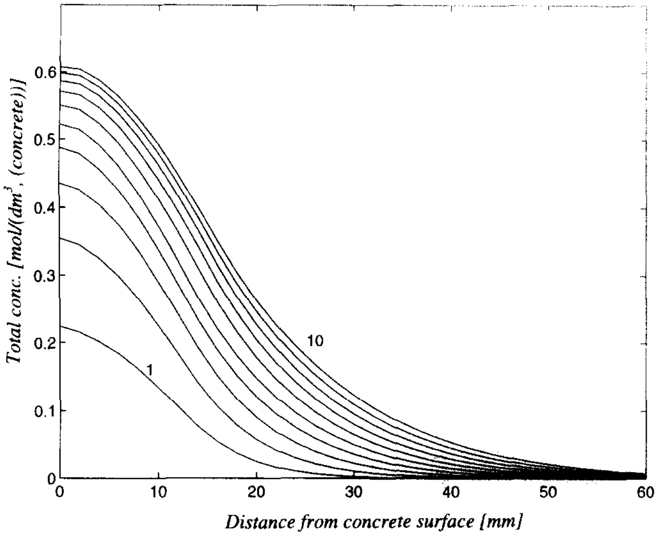

FIGURE 1. Case 1, total chloride content, i.e., the sum of C and F, 1–10 years.

Case 1 represents a situation where deicing salts, with a concentration $1.7\cdot10^{-3}$ [mol/m^3], are applied to the concrete surface 1 month a year. Between the deicing salt periods the outer climate is assumed to be dry without any salts present at the surface, i.e., the boundary conditions for C and θ_α (or the boundary conditions for the corresponding flows) are changed to simulate a deicing salt period and the drying period. Case 2 represents a situation where a constant exposure of salts at the concrete surface, with a concentration $1.7\cdot10^{-3}$ [mol/m^3], is applied. The results, in terms of chloride ion ingress at different times, are shown in Figures 1 and 2 (case 1) and Figures 3 and 4 (case 2). The material parameters used were: $k = 3.5\cdot10^{-4}$ [s^{-1}], $m = 1.2\cdot10^{-4}$

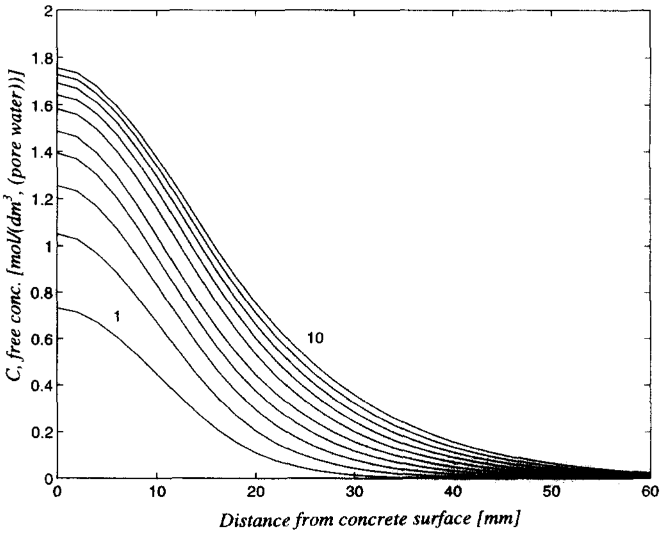

FIGURE 2. Case 1, free chloride content C, at different times, 1–10 years.

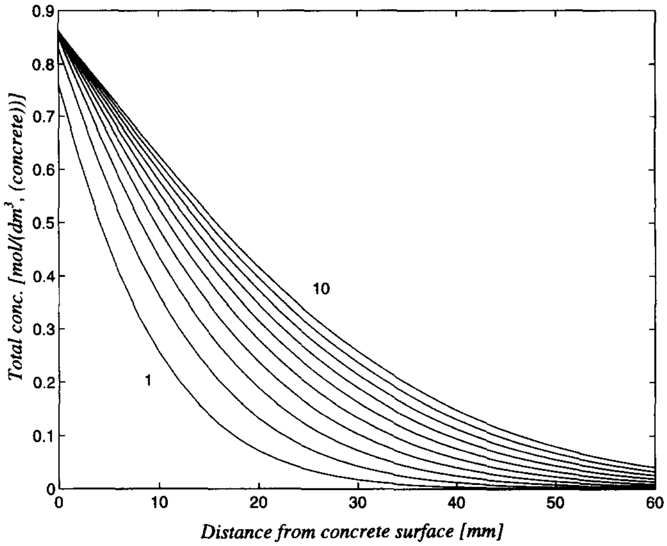

FIGURE 3. Case 2, total chloride content, i.e., the sum of C and F, 1–10 years.

[s^{-1}], $D_h(\theta_\alpha) = 5 \cdot 10^{-12}\ \theta_\alpha^2\ [m^2 s^{-1}]$, and $D_\alpha(\theta_\alpha)$ is chosen according to Hedenblad [8], which corresponds to a normal concrete, *v.c.t* = 0.5. The function $D_\alpha(\theta_\alpha)$ is not given explicitly, as the numerical computation is based on a transformation; however, the data used and information about the performed transformation can be found elsewhere [8,13]. A modification of the function $D_\alpha(\theta_\alpha)$ has also been introduced to be able to model the capillary suction phenomena.

The principal behavior of the chloride ingress for the two different cases is in good agreement with field measurements under such conditions [3]. The surface concentration increase in time in case 1 and the ingress of chlorides in case 1 are considerably high due to the convection phenomenon.

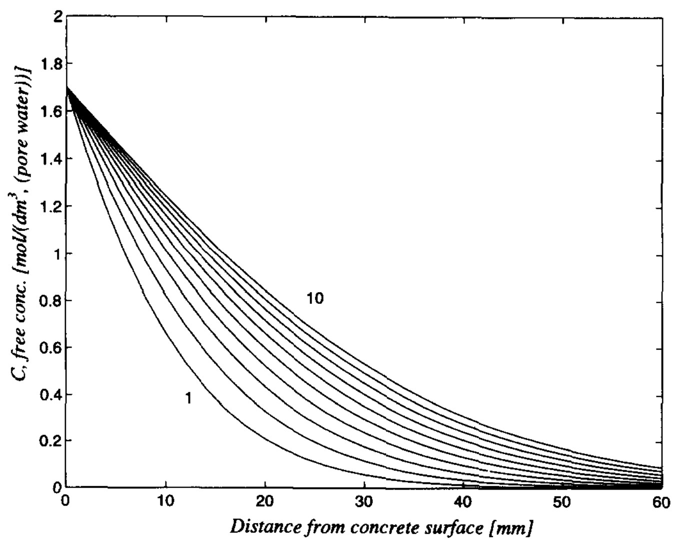

FIGURE 4. Case 2, free chloride content C, at different times, 1–10 years.

Conclusions

The ingress of pollutants into concrete can be modeled using equations describing diffusion, convection, and adsorption and desorption of the substance in question. To describe the most important physical phenomena one needs at minimum three equations: the equation describing mass balance for the pollutant together with constitutive relations; the equation describing mass balance for the pore water phase together with constitutive relations; and the equation describing the adsorption and desorption phenomenon. The crux is that the penetration of pollutants (such as chlorides) into concrete is described with different physical phenomena that are coupled. However, developing a model based on physically relevant phenomena will increase the possibilities of performing significant experiments. Furthermore, a powerful numerical method is needed to solve the equation system since no analytical solutions exist for this kind of problem, i.e., a set of coupled equations must be solved that should be compared with the global response obtained by experiments.

References

1. Bathe, K.J. *The Finite Element Procedures*; Prentice Hall: Englewood Cliffs, New Jersey, 1996.
2. Christie, I.; Griffiths, F.; Mitchell, A.R.; Zienkiewicz, O.C. *Int. J. Num. Meth. Eng.* **1976,** *10,* 1389–1396.
3. Sandberg, P. *Critical Evaluation of Factors Affecting Chloride Initiated Reinforcement Corrosion in Concrete*; Division of Building Materials, Lund Institute of Technology: Lund, Sweden, 1995.
4. Volkwein, A. *Untersuchungen über das Eindringen von Wasser und Chlorid in Beton,* Institute of building Materials, Technical University of Munich: Munich, Germany, 1991.
5. Bear, J. *Hydraulics of Groundwater, McGraw-Hill Series in Water Resources and Environmental Engineering*; McGraw-Hill: New York, 1979.
6. Bowen, R.M. In *Continuum Physics, Vol. 3*; Cemal Erigen, A, Ed.; Academic Press: New York, 1976, 2–127.
7. Tang, L. *Methods for Determining Chloride Diffusivity in Concrete*; Division of Building Materials, Chalmers University of Technology: Gothenburg, Sweden, 1993.
8. Hedenblad, G. *Moisture Permeability of Mature Concrete, Cement, Mortar and Cement Paste*; Division of Building Materials, Lund Institute of Technology: Lund, Sweden, 1993.
9. Bazant, Z.P. *J. Eng. Mech. Div., Proc. ASCE* **1979,** *105,* 1137–1166.
10. Truesdell, C.; Toupin, R.A. In *Handbuch der Physic, Vol. III-1*; Flügge, S., Ed.; Springer: Berlin, 1960, 226–793.
11. Hougan, O.A.; Marshall, W.R. *Chem. Eng. Prog.* **1947,** *43,* 197–208.
12. Tritthart, J. *Cem. Concr. Res.* **1989,** *19,* 683–691.
13. Arvidsson, J. *Isoterma fuktförlopp i porösa material*; Division of Building Physics, Lund Institute of Technology: Lund, Sweden, 1996.