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Modeling the influence of chemical reactions on the mechanisms of ionic transport in porous materials

An overview

E. Samson[a,b], J. Marchand[a,b,*], J.J. Beaudoin[c]

[a]*CRIB-Département de génie civil, Université Laval, Ste-Foy Quebec, Canada G1K 7P4*
[b]*SIMCO Technologies Inc., 1400, boul. du Parc Technologique, Quebec, Canada G1P 4R7*
[c]*Materials Laboratory, Institute for Research in Construction, National Research Council, Ottawa Ontario, Canada K1A 0R6*

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Abstract

This paper attempts to critically review various approaches developed to model the effects of chemical reactions on the mechanisms of ionic transport in porous media. A comprehensive overview of the various types of chemical reactions that can occur in reactive porous solids is first presented. Methods to model each of these chemical reactions are then described and analyzed. The ability of each of the proposed algorithms to predict the behavior of hydrated cement systems is discussed. The implementation of these algorithms in an ionic transport numerical model is also discussed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Concrete is a porous material made of a rigid solid skeleton and a liquid (or aqueous) phase. The solid is a composite mixture of ill-crystallized hydrated calcium silicates and other more crystalline phases. The liquid phase is a highly charged ionic solution containing mainly OH^-, K^+, Na^+, SO_4^{2-} and Ca^{2+} ions. Once the initial stages of hydration are completed, the liquid phase can be considered to be in a metastable state of thermodynamic equilibrium with the various solid phases.

During the service-life of the concrete structure, the chemical composition of the material pore fluid can be modified by the penetration of external ions and/or the leaching of ions already present in the pore solution. These ionic species can be transported by simple ionic diffusion or by a coupled process of capillary suction and diffusion. The modification of the pore solution chemical composition readily perturbs the local thermodynamic equilibrium of the system. A series of dissolution/precipitation reactions can occur to restore the equilibrium state.

An example reaction is the dissolution of calcium hydroxide, $Ca(OH)_2$. The reaction is initiated when the hydrated cement paste pore solution, initially at a pH of about 13.5, is in contact with an external solution at a lower pH. Hydroxyl ions in the material pore solution will tend to be leached out of the system under the electrochemical potential gradient. In order to restore the local equilibrium, calcium hydroxide will dissolve, thus releasing OH^- and Ca^{2+} ions in solution. Numerous concrete structures are exposed to this simple form of chemical degradation.

Concrete structures, such as bridges, harbors and offshore platforms, exposed to chloride solutions are also likely to suffer from another form of degradation. As a result of the concentration gradient between the hydrated cement paste pore solution and the external solution, chloride ions will penetrate into the material pore structure. The presence of chloride readily disturbs the equilibrium conditions between the pore solution and the paste. As a result, and under certain conditions, new solid phases, e.g. Friedel's salt, will precipitate to maintain equilibrium. Similar reactions can occur in hydrated cement systems exposed to sulfate and magnesium solutions. For instance, ettringite and gypsum are phases that can precipitate in hydrated cement systems exposed to sulfate solutions.

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* Corresponding author. Department of Civil Engineering, Laval University, Sainte-Foy, Quebec, Canada G1F 7P4. Tel.: +1-418-656-2079; fax: +1-418-656-3355.

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

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The proper modeling of these different chemical reactions is a problem of paramount importance for civil engineers and concrete technologists [1]. An adequate ionic and fluid transport model could predict the degradation of concrete structures with time. This would help engineers to properly design new structures and also allow good planning of maintenance programs. This aspect is particularly important since contractors are increasingly required to guarantee the durability of their structures for periods often as long as 90 years.

This paper attempts to critically review various approaches developed to model chemical reactions in porous media. The ability of each of the proposed algorithms to predict the behavior of hydrated cement systems is discussed.

2. Types of chemical reactions

In a comprehensive review on the modeling of chemical reactions in porous media, Rubin [2] distinguishes two main categories: sufficiently fast and reversible, and insufficiently fast and/or irreversible. If the rate of reaction is large with respect to the ionic and fluid transport processes, then it belongs to the sufficiently fast category [2]. In this particular case, the assumption is made that the local chemical equilibrium is preserved throughout the porous system. Only this first kind of chemical reaction will be considered in the following paragraphs. As emphasized by Barbarulo et al. [3], in most practical cases involving the diffusion of ions in fluid saturated systems, the local chemical equilibrium assumption is usually valid.

All reactions falling under the sufficiently fast category are modeled through chemical equilibrium equations [2], which are algebraic, as opposed to the partial differential equations used in transport models. Since the equilibrium is, in most cases, expressed through chemical activity, algebraic relations giving the chemical activity coefficients must also be considered while modeling the chemical reactions. The resolution of a transport problem involving chemical reactions is thus called a mixed problem, because it involves algebraic and partial differential equations.

According to Rubin [2], the chemical reactions are then divided into two subcategories: homogeneous and heterogeneous. The homogeneous reactions are those involving a single phase. This subcategory includes all the complexation reactions, i.e. the formation of products occurring in the aqueous phase. For example, the reaction [Eq. (1)]:

$$\mathrm{Ca^{2+}_{(aq)}} + \mathrm{OH^{-}_{aq}} \rightleftharpoons \mathrm{CaOH^{+}_{(aq)}} \tag{1}$$

is a homogeneous reaction since it only occurs in the aqueous phase.

As opposed to those falling in the previous category, the heterogeneous reactions involve at least two phases [2]. Rubin [2] distinguishes two types of heterogeneous reactions: surface and classical ones. Surface reactions are either adsorption, in which ions are attracted to the surface of the pore network under the influence of electrostatic forces [4], or ion exchange, in which two or more ionic species are exchanged between the surface of the solid and the aqueous phase [2]. The classical reactions are precipitation, dissolution, oxidation and reduction. The dissolution of calcium hydroxide, described in the introduction, belongs to this category since it involves the aqueous and the solid phase:

$$\mathrm{Ca^{2+}_{(aq)}} + 2\mathrm{OH^{-}_{(aq)}} \rightleftharpoons \mathrm{Ca(OH)_{2_{(s)}}} \tag{2}$$

3. Coupling chemical reactions to ionic transport in a saturated porous medium

In the following sections, each of the previous subcategories of chemical reactions will be treated in greater detail from the point of view of their implementation in an ionic transport model. In all the forthcoming examples, we will assume that the porous medium is kept in *isothermal* and *fluid saturated* conditions. For simplicity, we will assume that the ionic diffusion process can be described by Fick's law, which can be written in one dimension as:

$$\frac{\partial c_i}{\partial t} - D_i \frac{\partial^2 c_i}{\partial x^2} = 0 \tag{3}$$

where c_i is the concentration of the species i and D_i is the diffusion coefficient. This approximation is made to enable the reader to focus on the modeling of the chemical reactions. However, it is emphasized that Fick's law cannot accurately describe the ionic diffusion process in hydrated cement systems [5].

4. Treatment of homogeneous chemical reactions

The treatment of homogeneous chemical reactions is reviewed first. Consider the aqueous phase of a porous network in which the ions $\mathrm{Ca^{2+}}$, $\mathrm{OH^{-}}$, $\mathrm{Na^{+}}$ and $\mathrm{Cl^{-}}$ undergo, for example, the following reactions [Eqs. (4) and (5)]:

$$\mathrm{Ca^{2+}_{(aq)}} + \mathrm{OH^{-}_{(aq)}} \rightleftharpoons \mathrm{CaOH^{+}_{(aq)}} \tag{4}$$

$$\mathrm{Ca^{2+}_{(aq)}} + \mathrm{Cl^{-}_{(aq)}} \rightleftharpoons \mathrm{CaCl^{+}_{(aq)}} \tag{5}$$

Let us define c_1 as the concentration of $\mathrm{Ca^{2+}}$, c_2 as the concentration of $\mathrm{OH^{-}}$, c_3 as the concentration of $\mathrm{Cl^{-}}$ and c_4 as the concentration of $\mathrm{Na^{+}}$. Following that, the complexes are expressed as c_{12} for $\mathrm{CaOH^{+}}$ and c_{13} as $\mathrm{CaCl^{+}}$. The equilibrium relations for each of these chemical reactions are given by [2]:

$$K_1 = \frac{\gamma_1 c_1 \gamma_2 c_2}{\gamma_{12} c_{12}} \tag{6}$$

$$K_2 = \frac{\gamma_1 c_1 \gamma_3 c_3}{\gamma_{13} c_{13}} \tag{7}$$

where the γ_i's are the chemical activity coefficients. These coefficients can be calculated with various models, e.g.

Debye–Hückel or Davies, depending on the ionic strength of the pore solution [6]. For the specific case of cement-based materials, which contain a highly charged pore solution, the previous models are inadequate. The following expression, a modification of Davies' relationship, was found to yield good results [7]:

$$\ln\gamma_i = -\frac{Az_i^2\sqrt{I}}{1+a_iB\sqrt{I}} + \frac{(0.2-4.17\times10^{-5}I)Az_i^2I}{\sqrt{1000}} \tag{8}$$

where I is the ionic strength of the solution (Eq. (9)):

$$I = 0.5\sum_{i=1}^{N} z_i^2 c_i \tag{9}$$

z_i being the valence number of a given ionic species and N is the total number of ionic species in the aqueous solution. In Eq. (8), A and B are temperature-dependent parameters, given by [Eqs. (10) and (11)]:

$$A = \frac{\sqrt{2}F^2 e_o}{8\pi(\epsilon RT)^{3/2}} \tag{10}$$

$$B = \sqrt{\frac{2F^2}{\epsilon RT}} \tag{11}$$

where F is the Faraday constant, e_o is the electrical charge of one electron, $\epsilon=\epsilon_r\epsilon_o$ is the permittivity of the medium, given by the dielectric constant times the permittivity of the vacuum, R is the ideal gas constant and T is the temperature. Finally, the parameter a_i in Eq. (8), often compared to an ionic radius, is specific to the ionic species. Its value (in meters, m) is 3×10^{-10} for OH^-, 3×10^{-10} for Na^+, 2×10^{-10} for Cl^- and 1×10^{-13} for Ca^{2+} [7].

Following this set of algebraic equations for the chemical equilibrium, mass conservation equations have to be considered for the transport of each ionic species. As previously stated, we will assume that the ionic diffusion process can be described by Fick's law [Eq. (3)]:

$$\frac{\partial c_1}{\partial t} = D_1\frac{\partial^2 c_1}{\partial x^2} \tag{12}$$

$$\frac{\partial c_2}{\partial t} = D_2\frac{\partial^2 c_2}{\partial x^2} \tag{13}$$

$$\frac{\partial c_3}{\partial t} = D_3\frac{\partial^2 c_3}{\partial x^2} \tag{14}$$

$$\frac{\partial c_4}{\partial t} = D_4\frac{\partial^2 c_4}{\partial x^2} \tag{15}$$

$$\frac{\partial c_{12}}{\partial t} = D_{12}\frac{\partial^2 c_{12}}{\partial x^2} \tag{16}$$

$$\frac{\partial c_{13}}{\partial t} = D_{13}\frac{\partial^2 c_{13}}{\partial x^2} \tag{17}$$

The complete system of equations therefore consists of the two chemical equilibrium equations [Eqs. (6) and (7)], five chemical activity relations corresponding to Eq. (8) (one for each species except for Na^+, which does not appear in the chemical equilibrium equations), and the six transport equations [Eqs. (12)–(17)], a total of 13 equations. There are 11 unknowns, the six concentrations and five chemical activity coefficients (again, one for each species except Na^+).

To have a closed system, i.e. a system in which there is the same number of unknowns as there are equations, it is possible to reduce the number of equations by applying the mass conservation principle over the total mass of a given component, even if it appears in different species. It means, for example, to consider calcium in Ca^{2+}, $CaOH^+$ and $CaCl^+$ [2]. This leads to the following set of mass conservation equations:

$$\frac{\partial c_1}{\partial t} + \frac{\partial c_{12}}{\partial t} + \frac{\partial c_{13}}{\partial t} = D_1\frac{\partial^2 c_1}{\partial x^2} + D_{12}\frac{\partial^2 c_{12}}{\partial x^2} + D_{13}\frac{\partial^2 c_{13}}{\partial x^2} \tag{18}$$

$$\frac{\partial c_2}{\partial t} + \frac{\partial c_{12}}{\partial t} = D_2\frac{\partial^2 c_2}{\partial x^2} + D_{12}\frac{\partial^2 c_{12}}{\partial x^2} \tag{19}$$

$$\frac{\partial c_3}{\partial t} + \frac{\partial c_{13}}{\partial t} = D_3\frac{\partial^2 c_3}{\partial x^2} + D_{13}\frac{\partial^2 c_{13}}{\partial x^2} \tag{20}$$

$$\frac{\partial c_4}{\partial t} = D_4\frac{\partial^2 c_4}{\partial x^2} \tag{21}$$

These four transport equations, combined with the two chemical equilibrium relations and the five chemical activity relationships, form a set of 11 equations, matching the number of unknowns.

Two different techniques are used to solve this system of equations. In the first one, the algebraic and partial differential equations are solved altogether [8–10]. This technique is called the coupled method. The discretization of this system of equations with either the finite difference or the finite element technique will lead to very large systems of equations because of the large number of unknowns at each nodal point.

In the second technique, the partial differential equations and the algebraic ones are uncoupled [8,11]. This is performed first by introducing a new set of variables [2,8]:

$$u = c_1 + c_{12} + c_{13} \tag{22}$$

$$v = c_2 + c_{12} \tag{23}$$

$$w = c_3 + c_{13} \tag{24}$$

Since the operators $\partial(.)/\partial t$ and $\partial^2(.)/\partial x^2$ are linear, and assuming a constant diffusion coefficient D for all the species, it is possible to substitute Eqs. (22)–(24) in Eqs. (18)–(20) to yield the following equations [Eqs. (25)–(27)]:

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2} \tag{25}$$

$$\frac{\partial v}{\partial t} = D\frac{\partial^2 v}{\partial x^2} \tag{26}$$

$$\frac{\partial w}{\partial t} = D\frac{\partial^2 w}{\partial x^2} \tag{27}$$

Combined with Eq. (21), this constitutes a set of independent equations, which can be solved separately [2]. Once u, v and w are known at a given time t and for any position x, a system of 10 algebraic nonlinear equations, i.e. Eqs. (6) and (7), five equations [Eq. (8)] for chemical activity coefficients and Eqs. (22)–(24), is solved at given locations. These locations could be nodal points if a numerical method like finite differences or finite elements is used.

The strong argument in favor of this second technique is a reduction of the size of the system of equations to solve, a reduction which is more dramatic as the size of the problem considered is increased. However, it suffers from two important drawbacks. The operators controlling the transport of the ions have to be linear. It thus prevents the use of a more sophisticated model, like the extended Nernst–Planck equation [12], which takes into account the electrical coupling between each ion and the chemical activity effects. Furthermore, the assumption that all species must have the same diffusion coefficient may not always be valid.

5. Treatment of surface chemical reactions

The second class of chemical reactions reviewed concerns heterogeneous reactions involving surface phenomena. This means that ions are exchanged between the solution and the surface of the solid phase. Consider a solid phase $X_{(s)}$ on which a given number of sites are available for cations. Taking the same ions in aqueous phase as in the homogeneous example, OH^-, Ca^{2+}, Na^+ and Cl^-, this means that Ca^{2+} and Na^+ will compete for the available sites. The exchange between Na^+, Ca^{2+} and the solid phase can be written as [2] [Eq. (28)]:

$$2Na^+_{(aq)} + CaX_{(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2NaX_{(s)} \tag{28}$$

where the subscript (s) stands for the solid phase. For that kind of chemical reaction, the equilibrium constant is given by [2,13]:

$$K = \left(\frac{c_4^{(s)}}{c_4}\right)\left(\frac{c_1}{c_1^{(s)}}\right)^2 \tag{29}$$

The other algebraic equation required to describe the chemical reaction is given by the definition of the ion-exchange capacity $c_T^{(s)}$ [13,14], which gives the total amount of sites available on the solid for exchanges with the aqueous phase [Eq. (30)]:

$$c_T^{(s)} = \sum_{i=1}^{n} c_i^{(s)} \tag{30}$$

where n is the number of exchanging ions. The ion-exchange capacity is assumed to be a constant fixed value [14]. For the particular example corresponding to Eq. (29), the ion-exchange capacity is given by:

$$c_T^{(s)} = c_1^{(s)} + c_4^{(s)} \tag{31}$$

To this set of algebraic equations, the transport equations must be added. Since ions 2 and 3 (OH^- and Cl^-) do not participate in the ion exchange described here, Eqs. (13) and (14) can be solved independently to find concentrations c_2 and c_3. For Na^+ and Ca^{2+}, a term is added in the transport equation to account for the exchange between the aqueous and the solid phase [15]:

$$(1-\phi)\frac{\partial c_1^{(s)}}{\partial t} + \phi\frac{\partial c_1}{\partial t} = \phi D_1\frac{\partial^2 c_1}{\partial x^2} \tag{32}$$

$$(1-\phi)\frac{\partial c_4^{(s)}}{\partial t} + \phi\frac{\partial c_4}{\partial t} = \phi D_4\frac{\partial^2 c_4}{\partial x^2} \tag{33}$$

where ϕ is the porosity of the material, assumed constant.

The combination of the two transport equations [Eqs. (32) and (33)] with the algebraic equations [Eqs. (29) and (31)] give a system of four equations and four unknowns. But it is possible to reduce that number to two equations and two unknowns [13,14] by first combining the two algebraic equations, which will give a relation of the form:

$$c_i^{(s)} = f(c_1, c_2, \ldots, c_n) \text{ for } i = 1, 2, \ldots, n \tag{34}$$

This expression is called an exchange (or interaction) isotherm. It can be substituted in the proper transport equation by applying the chain rule to the time derivative of the solid concentration [Eq. (35)]:

$$\frac{\partial c_i^{(s)}}{\partial t} = \frac{\partial c_i^{(s)}}{\partial c_1}\frac{\partial c_1}{\partial t} + \frac{\partial c_i^{(s)}}{\partial c_2}\frac{\partial c_2}{\partial t} + \ldots + \frac{\partial c_i^{(s)}}{\partial c_n}\frac{\partial c_n}{\partial t} \text{ for } i = 1, 2, \ldots, n \tag{35}$$

This technique, applied to the example described by Eqs. (29) and (31) leads to:

$$c_1^{(s)} = -\frac{c_1^2}{2Kc_4} \pm \frac{1}{2}\sqrt{\frac{c_1^4}{K^2c_4^2} + \frac{4c_T^{(s)}c_1^2}{Kc_4}} \tag{36}$$

Depending on the values of the parameters in this relationship, only one root will have a physical meaning [13]. Eq. (36) can be substituted into Eq. (32) through the chain rule. By finding a similar expression for $c_4^{(s)}$, the initial system of four equations is reduced to two equations and two unknowns.

Before concluding this discussion on heterogeneous surface reactions, it is worth mentioning a special case. In some specific cases, the sum of the concentrations of the various ions in the aqueous phase involved in the ion-exchange process is a constant. For the case of two monovalent ions involved in such a situation, the following expression can be written [Eq. (37)]:

$$c_T = c_1 + c_2 \tag{37}$$

where c_T has a known constant value. For this case, the equilibrium constant and the ion-exchange capacity would be [Eqs. (38) and (39)]:

$$K = \frac{c_1^{(s)}}{c_1}\frac{c_2}{c_2^{(s)}} \tag{38}$$

$$c_T^{(s)} = c_1^{(s)} + c_2^{(s)} \tag{39}$$

The combination of these three expressions gives the following relationship:

$$c_1^{(s)} = \frac{Ac_1}{1 + Bc_1} \text{ with } A = \frac{Kc_T^{(s)}}{c_T} \text{ and } B = \frac{K-1}{c_T} \tag{40}$$

One can recognize in this expression the familiar single-component Langmuir isotherm [13,15]. It is sometimes used to model the chemical reactions involving chloride ions in cement-based materials [16].

It should be emphasized that the previous approach is based on the assumption that the exchange capacity of the surface remains constant. Although it might be verified in certain instances, this hypothesis is unrealistic in most practical cases that involve the transport of OH^- ions through the material pore structure. The reduction in the pH of the pore solution is known to have a strong influence on the composition and structure of the C-S-H gel [17]. Evidence of interactions between ions and C-S-H gel reported in the literature suggest the ion-solid sorption binding coefficient depends on both the Ca:Si ratio within the C-S-H and the composition of the pore solution [18–20].

Numerous more sophisticated approaches (such surface protonation models) have been developed to describe surface exchange mechanisms [21,22]. The main problem with these models is that the interaction mechanisms are described at the very local scale. These equations are usually difficult to homogenize over the scale of the porous solid.

6. Treatment of dissolution/precipitation reactions

The last category concerns the heterogeneous chemical reactions involving precipitation, dissolution, oxidation or reduction processes. In this paper, only dissolution and precipitation are considered. Such a reaction was already described by Eq. (2). The algebraic chemical equilibrium equation used to model these reactions is similar to those of the homogeneous or heterogeneous surface reactions, Eqs. (6), (7) and (29). For the chemical reaction [Eq. (2)], the relationship is [8,23]:

$$K = \gamma_1 c_1 \gamma_2^2 c_2^2 \tag{41}$$

But the similarity with the other chemical equilibrium relationships hides huge differences. For Eqs. (6), (7) and (29), the relationship between the various components of the chemical reactions always applies. Furthermore, all components involved in the chemical reaction are considered in the equilibrium relationship. For the heterogeneous dissolution/precipitation process, the solid phase concentration does not appear in Eq. (41). Furthermore, when there is no solid, the product of the activity [Eq. (41)] can be lower than *K*. So it is more precise to express it as an inequality [23] [Eq. (42)]:

$$\gamma_1 c_1 \gamma_2^2 c_2^2 \begin{cases} = K \text{ if the precipitate is present} \\ < K \text{ if there is no precipitate} \end{cases} \tag{42}$$

This inequality allows the precipitate concentration to be discontinuous in the material [8]. Suppose the usual ions (Ca^{2+}, OH^-, Na^+ and Cl^-) are initially in equilibrium with a material containing the solid $Ca(OH)_2$ and are allowed to leach out of the porous network. Initially, the concentration of Ca^{2+} and OH^- obeys the relationship [Eq. (41)] since the solid phase is present. At the surface of the material, the product $\gamma_1 c_1 \gamma_2{}^2 c_2{}^2$ will eventually be lower than its initial value. The solid will thus dissolve, putting back Ca^{2+} and OH^- ions in solution to reach equilibrium again, until there is no more solid at this location. Subsequently, the same process will occur right next to the previous location. The solid concentration will thus behave like a moving boundary [2], in this case moving in the direction opposite to the leaching of the ions.

The mass conservation equations will be affected by the discontinuous behavior of this type of chemical reaction. Ions Cl^- and Na^+, associated with concentrations c_3 and c_4, are not affected by the reaction. Hence, their transport can be modeled with Eqs. (14) and (15) at any location in the material. For ions Ca^{2+} and OH^-, the situation is different. In the zone where the precipitate concentration is zero, the transport of these species obeys Eqs. (12) and (13). Elsewhere, precipitate is present and Ca^{2+} follows Eq. (32). For OH^-, the equation is similar:

$$(1-\phi)\frac{\partial c_2^{(s)}}{\partial t} + \phi\frac{\partial c_2}{\partial t} = \phi D_2 \frac{\partial^2 c_2}{\partial x^2} \tag{43}$$

Three techniques have been developed to solve this type of problem. The first, fully described in Refs. [24,25], separates the porous material into *k* zones of constant mineralogical properties and solves the transport equations in each zone with the proper conservation equations at the moving boundary interfaces. The mathematics of this technique is described in the following paragraphs.

First, let us define the function ζ as [Eq. (44)]:

$$\zeta_k(x,t) = \begin{cases} 1 \text{ if } x \text{ is in zone } k \\ 0 \text{ elsewhere} \end{cases} \tag{44}$$

For unidimensional cases, k also designates one of the interfaces adjacent to a given zone. Next, the variables appearing in the transport equations, namely the concentrations in both the aqueous and the solid phase, are expressed as functions of ζ [Eq. (45)]:

$$c_i = \sum_{k=1}^{N_\Xi} c_i^k \zeta_k \tag{45}$$

where N_Ξ is the total number of zones. The derivative of ζ introduces jumps or discontinuities in the transport equations. For the concentrations, which have to be continuous at the interfaces, these jumps are set to zero, which yields for example [Eq. (46)]:

$$\frac{\partial c_i}{\partial t} = \sum_{k=1}^{N_\Xi} \frac{\partial c_i^k}{\partial t} \zeta k \tag{46}$$

But certain quantities, like fluxes, are allowed to show some discontinuity at the interfaces. For example, the space derivative of a flux is given by [Eq. (47)]:

$$\frac{\partial j_i}{\partial x} = \sum_{k=1}^{N_\Xi} \frac{\partial j_i^k}{\partial x} \zeta_k + \sum_{k=1}^{N_\Xi = -1} [j_i]_k \delta(x - x_k) \tag{47}$$

where $[\ldots]_k$ represents the jump of the function in the square brackets across a given interface, x_k is the position of the interface and $\delta(x - x_k)$ is the Dirac delta function, defined as [Eq. (48)]:

$$\delta(x - x_k) = \begin{cases} 1 \text{ if } x = x_k \\ 0 \text{ if } x \neq x_k \end{cases} \tag{48}$$

The transformations applied to the transport equations in order to consider the dissolution or the precipitation reactions at various interfaces introduce a new variable: the position x_k of these interfaces.

To take into account this new variable, another equation has to be introduced in the system. It is obtained by performing mass conservation across a given interface. The resulting relationship is called the generalized Rankine–Hugoniot equation [24] [Eq. (49)]:

$$\phi [j_i]_k = [c_{is}]_k \frac{\mathrm{d}x_k}{\mathrm{d}t} \tag{49}$$

presented here for a case where the porosity ϕ is considered constant.

The complete system of equations is thus made up from the proper transport equations within each zone of constant mineralogical properties, to which are added the Rankine–Hugoniot equations at the various interfaces.

Although mathematically sound, this technique creates complications from a numerical point of view. Not only does it add a new variable and the corresponding equation to the transport model, but the division of the material into zones of constant chemical properties requires the storage of a large amount of information since the Rankine–Hugoniot equation must be solved at each interface. The transport equations are also different depending on the zone in which they are applied. This requires a very complex algorithm.

The second technique used to solve dissolution/precipitation problems combines the algebraic equations for chemical equilibrium with the partial differential transport equations to form a global system of equations [23], in a manner similar to that for the first technique involving homogeneous reactions. In such a system, there are two equations for transport [Eqs. (32) and (43)], the chemical equilibrium equation [Eq. (41)] and two equations similar to Eq. (8) for the chemical activity coefficients, a total of five equations. Correspondingly, there are six unknowns: two concentrations in aqueous phase c_1 and c_2, two concentrations in solid phase, $c_1^{(s)}$ and $c_2^{(s)}$, and the two chemical activity coefficients γ_1 and γ_2. One unknown is eliminated by knowing that in the solid $Ca(OH)_2$, $c_2^{(s)} = 2c_1^{(s)}$, closing the system. Finally, the chemical equilibrium relationship is presumed not to be in effect initially, and it is checked at each node every iteration and is either "turned-on" or "turned-off" appropriately [23].

The last technique consists in uncoupling the transport and the chemical reactions [26]. In the first step of calculation, the concentration profiles of the various species are calculated with a transport model, such as the Fick or the extended Nernst–Planck models. The calculation is performed without taking into account chemical reactions, i.e. the term $(1 - \phi)\ (\partial c^{(s)})/(\partial t)$, is not considered. After that step, the concentrations at a given node are checked to see if they violate the chemical equilibrium relationships of the various chemical reactions considered. If this is the case, they are brought back to equilibrium with a separate chemical code. If dissolution or precipitation occurs, the solid phases are modified appropriately. This procedure is repeated for every nodal point. After that operation, the modified concentration profiles serve as a starting point for the calculation of the next time step.

This algorithm is interesting because it allows for the use of very complex chemical equilibrium codes. The main problem of this model is that in order for the dissolution or the precipitation of the solid phases to show moving fronts, the time steps used in the calculation must be short. If they are too large, the reactions will occur on a wide area, and not on thin fronts.

7. Discussion and concluding remarks

This completes the review on the modeling of the three main types of chemical reactions that can occur in a porous material under the local equilibrium assumption. Even though they were presented separately, they occur simultaneously in most real life situations. Most of the models found in the literature consider complexation and adsorption, but overlook the dissolution/precipitation reactions [9–11,27,28].

This is easily understandable since the latter reactions are much more complicated to model, because of the discontinuous aspect of the chemical equilibrium equation. Nevertheless, some models consider the three types of reactions, as those in references [23,26,29]. But in these three cases, only one solid phase is taken into account. Finally, it is worth mentioning that all the models previously discussed were developed by geochemists and hydrogeologists.

Very little research has been specifically focused on the treatment of chemical reactions in hydrated cement systems. This is most unfortunate since these materials are quite different from other porous solids. For instance, cement-based materials are characterized by the relatively high ionic strength of their pore solution [30]. This has an important influence on the transport, since the contact with the external environment will often induce very strong concentration gradients. Ions like OH^- and Ca^{2+}, which have very different diffusion coefficients, 5.273×10^{-9} and 0.792×10^{-9} m^2/s in free water, respectively, are very likely to experience an internal electrical potential that will arise to maintain electroneutrality by slowing the fast ions and accelerating the slow ones [31]. Hence, the simple Fick's law is no longer appropriate and more complex models, like the Nernst–Planck or extended Nernst–Planck equations [32,33] should be used.

Cement-based materials are also characterized by the high reactivity of the hydrated cement paste. Aside from the dissolution of portlandite, which has already been described, other chemical reactions will occur, for example, the decalcifiation of the C-S-H, the formation of ettringite under external sulfate attack or the formation of Friedel's salt upon chloride penetration in the porous network. Over the past decades, numerous reports have clearly emphasized the significant influence of these dissolution/precipitation reactions on the durability of hydrated cement systems. Although complexation and ion adsorption phenomena can occur in a cement paste, they are likely to have a lesser influence on the ionic transport and on the degree of degradation of cement-based materials.

Over the past decade, researchers in the field of ionic transport have relied on simple models to treat chemical reactions in cement systems. Chemical reactions are usually modeled using chemical interaction isotherms. This technique is essentially an adaptation of the mathematical approach used to treat heterogeneous surface reactions [see Eq. (34)].

Recently, the isotherm technique has been mainly used to model the chemical reactions on-going during the penetration of chloride in concrete. The experimental procedure, described in Ref. [34], shows that all types of reaction, i.e. dissolution/precipitation, complexation and adsorption, are described by one isotherm. The latter is then used in a single-ion transport model to yield chloride profiles in the material. For instance, Masi et al. [16] modeled the chloride interaction with a Langmuir isotherm [see Eq. (40)], whereas Saetta et al. [35] modeled the same reaction with the linear isotherm $c^{(s)} = Ac$. The main interest in this method lies in its simplicity. However, it is also its main drawback, since it is nearly impossible to correctly model complicated reactions involving multiple ionic species while considering only one ion. This is supported by the fact that, in the two papers mentioned previously, the same chemical reaction is modeled differently.

One attempt has been made by Adenot [36] to model dissolution/precipitation reactions in cement-based materials using a technique developed by Lichtner et al. [24,25], where the material is divided into zones of constant mineralogical properties. While it is an important improvement over the isotherm method, the heavy mathematics of this approach usually requires a simplification of the transport model. In his work, Adenot used Fick's law as the transport model, with all ions having the same diffusion coefficient. Furthermore, the equations are solved over a 1-D semi-infinite domain.

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