Modelisation of chloride reactive transport in concrete including thermodynamic equilibrium, kinetic control and surface complexation

Van Quan Tran[a], Anthony Soive[b,*], Véronique Baroghel-Bouny[c]

[a] Institute For Hydraulic Construction, No. 54 Trieu Khuc Street, Thanh Xuan District, Hanoi, Vietnam
[b] Cerema, UMR 7329 GEOAZUR, Pôle d'activités, avenue Albert Einstein CS 70499, Aix-en-Provence cedex 3 13593, France
[c] Paris-Est University, IFSTTAR, MaSt/FM2D, Marne-la-Vallée F-77447, France

ARTICLE INFO

ABSTRACT

In this study, a new physically and chemically based model taking into account thermodynamic equilibrium, kinetics and surface complexation is proposed to predict the ingress of chloride ions into saturated concretes. The numerical results of this multi-ionic model are compared to experimental data such as total and free chloride concentration profiles and chloride binding isotherms. With only one set of parameters, the results show very good agreement for chloride binding isotherm of concretes with different w/b, types of binders (CEM I, CEM III, and CEM I with fly ash) and various exposure conditions (NaCl solution at different concentrations). Such a model overcomes the use of empirical chloride binding isotherms that can be difficult to asses for concretes with supplementary cementitious materials. The very good results underline the need to take into account all the physical and chemical phenomena included in the model.

1. Introduction

The main cause of deterioration for reinforced concrete structures exposed to marine environments is corrosion induced by chloride penetration into concrete. Owing to the expensive costs of maintenance and repair there is a great demand for reliable models designed to predict chloride ingress and its consequences in term of corrosion.

Furthermore, a number of authors consider that the initiation stage of corrosion depends on a chloride threshold value which can be expressed in different forms, such as total chloride content relative to the weight of cement (or concrete) [1], free chloride content [2] and the commonly-used ratio $[Cl^-]/[OH^-]$ [3-5]. However, all of these descriptions are dependent not only on the propagation of the aggressive solution in the concrete but also on physicochemical reactions such as mineral dissolution/precipitation, sorption/desorption onto mineral surface and aqueous complexation reactions. A reactive transport model could take into account all of these mechanisms.

A number of chloride transport models can be found in the literature, such as models based on Fick's second law or multispecies ionic transport equations [6-8], or physically and chemically coupled model [9]. These models use global binding isotherms to determine total chloride amounts as a function of free chloride amounts. However, the parameters of these isotherms need to be calibrated directly with experimental data [7]. These parameters can also be deducted from the

C_3A content [10] or from the C_3A_{eq} and C-S-H content ([11] for example). However, in all cases, the parameters are specific to each concrete or to each type of cement. Using physically and chemically based model, Elakneswaran et al. [12] proposed to describe the adsorption of chloride ions more accurately. In their model, the mineral dissolution/precipitation of species in hydrated cement paste is firstly simulated by thermodynamic equilibrium in coupled reactive transport equations. Furthermore, the model takes into account the "physical" adsorption (or sorption/desorption onto a mineral surface) by a surface complexation model. This model describes binding of the ions on the mineral surface assumed as C-S-H. Elakneswaran et al. [12] successfully predicted the total chloride concentration profile in the case of sample exposed to artificial seawater for 91 days at 20 °C.

A number of reactive transport models is proposed in the literature to predict the durability of cementitious materials in chloride environments [13] or sulfate environment [14-19]. The authors assume that the various cement hydrates are in thermodynamic equilibrium. Assuming thermodynamic equilibrium implies that the chemical reaction is instantaneous. Consequently, the mineral species transform immediately [12,16,18-20]. However, taking into account mineral dissolution/precipitation kinetics seems to have a significant influence [21-23].

To the authors' knowledge, a coupled thermodynamic equilibrium/ kinetic and surface complexation has not been proposed to predict the

---

* Corresponding author.
E-mail address: anthony.soive@cerema.fr (A. Soive).

ingress of chloride ions into concrete with different w/b, types of binders, incorporation of supplementary cementing materials (SCMs) and exposure to various NaCl solution concentration. Therefore, in this paper a model including thermodynamic equilibrium, kinetic control and surface complexation is proposed. The model requires only one parameter (sorption density), whose value is the same for all concretes investigated (mixed with CEM I, CEM III or fly ash). The numerical results are firstly compared to experimental chloride binding isotherms. Two approaches for the mineral dissolution/precipitation - thermodynamic equilibrium (TE) and thermodynamic/kinetic (TK) - are then investigated. In TE, the reaction of all solid species is assumed to be instantaneous. The dissolution of some solid species is governed by kinetic laws in TK. The numerical total and free chloride concentration profiles are finally compared to experimental profiles.

In this paper, the first section depicts the governing equations used in the proposed reactive transport model in saturated cementitious materials, such as transport equations, surface complexation onto a mineral surface descriptions, the principle of thermodynamic equilibrium and kinetic laws. The second section introduces the input data of the model: parameters of solid species under kinetic constraint, parameters of surface complexation, initial mineralogical composition of the material, exposure conditions and numerical procedure. A sensitivity study of surface complexation parameter is carried out in order to calibrate the parameter in the third section. Model results are then compared to experimental data taken from [11] and discussed in the last section of the paper.

2. Description of the reactive transport model

2.1. Transport equations

In a saturated environment without convection phenomena, ion transport is governed by diffusion. Therefore, the principle of mass balance equation can be written in a general form in one-dimension model:

$$\frac{\partial M_j}{\partial t} = -\frac{\partial J_j}{\partial x} + q_j \tag{1}$$

M_j, J_j and x denote the molar accumulation of species j in the aqueous phase (mol·m^{-3} of material), the flux of species j in solution (mol·m^{-2}·s^{-1}) and the distance of diffusion (m), respectively. The q_j source or sink of species (mol·m^{-3}·s^{-1}) is interpreted by the removing or the releasing of species j through physical adsorption onto C-S-H surface (see Paragraph 2.2) $q_{j,C-S-H}$, mineral dissolution/precipitation $q_{j,s}$ and aqueous complexation in solution $q_{j,l}$.

Therefore, the source or sink of species is described as:

$$q_j = q_{j,C-S-H} + q_{j,s} + q_{j,l} \tag{2}$$

In porous media, considering the ionic interactions are taken into account in the source term, the flux of a species j, J_j, can be described by the first Fick's law:

$$J_j = -D_e \frac{\partial C_j}{\partial x} \tag{3}$$

$$D_e = \tau \phi D_{j,w} \tag{4}$$

where D_e is the effective diffusion coefficient of species j (m^2·s^{-1}), τ the tortuosity of the porous medium, ϕ the bulk porosity, $D_{j,w}$ the free water diffusion coefficient of species j (m^2·s^{-1}). C_j denotes the molar concentration of free species j in a pore solution (mol·dm^{-3} of solution). In this study as in other studies or software [25-30], the effective diffusion coefficient is assumed to be the same for all species, in

particular for primary species that are accounted for in the transport step (Cl$^-$, SO$_4^{2-}$, Al^{3+}, Na$^+$, K$^+$). The diffusion coefficients are assumed to be independent of composition and should be identical to maintain the consistency of model when the classical Fick's law is used. The velocity of the primary species is then the same. That implies zero current in this step. This method has the benefit of improving the calculation speed which can be important in order to study durability of lot of structures with different concretes. Of course, the main drawback of such a strong hypothesis is that it is unavailable when applying an electrical current on the sample boundary. In addition, as captured in geochemical transport codes at the present time, an electrical current typically arises due to the diffusion of charged species at different rates. Here again, the model is not able to catch this effect. Nevertheless, the model focuses on the chemical part of the reactive transport phenomenon taking into account electrical double layer, ionic complexation and dissolution and precipitation of solid species (with kinetics).

In fact, Fick's law is a strictly phenomenological relationship that is more rigorously treated with the Poisson-Nernst-Planck equation [31]. Several studies on reactive transport model that use such a model can be found in the literature (e.g. [9,16,18]). The advantage is to ensure charge balance in the transport part. Another way is to assume zero current which leads to a modified coupled Fick's law [24].

According to [31], the mineral dissolution/precipitation leads to bulk porosity reduction as follows:

$$\phi = 1 - \sum_{m=1}^{N_m} fr_m - fr_u \tag{5}$$

where fr_m is the volume fraction of mineral m in the medium ($V_{mineral}/V_{medium}$) and fr_u is the volume fraction of nonreactive medium. The porosity changes lead to effective diffusion changes.

The molar accumulation of species j is calculated as: $M_j = \phi C_j$. Therefore, Eq. (1) can be rewritten:

$$\frac{\partial \phi C_j}{\partial t} = D_e \frac{\partial^2 C_j}{\partial x^2} + q_{j,C-S-H} + q_{j,s} + q_{j,l} \tag{6}$$

It should be noted that the interactions between chemical reactions and transport phenomena are strong since ϕ and D_e depend on mineral dissolution/precipitation (see Eqs. (4) and (5)).

2.2. Interaction between solution and C-S-H surface by surface complexation model

In cementitious materials, the physical adsorption of ions onto the surface of the mineral species of concrete, in particular C-S-H, has been the subject of several studies [34-36]. The surface complexation model describes chemical reaction between the aqueous species and the specific surface sites. The most common surface complexation model is the double diffuse layer model described in detail by Dzombak and Morel [37]. The authors consider that the surface charge density is calculated from the total surface sites of the layer:

$$\sigma = F[\Gamma_H - \Gamma_{OH} + \sum (z_M \Gamma_M) + \sum (z_A \Gamma_A)] \tag{7}$$

where σ, F and z_i denote the surface charge density (C·m^{-2}), the Faraday constant (96,485 C·mol^{-1}) and the valance of sorbing ions i, respectively. Γ_H, Γ_{OH}, Γ_M and Γ_A are the sorption densities of surface sites (mol·m^{-2}) for protons, hydroxyl, sorbed cations an anions, respectively.

For example, if four kinds of charges in the surface layer are considered ($\equiv$ OH$_2^+$, $\equiv$OH, $\equiv$ OM$^+$, $\equiv$ OA$^-$) σ is calculated as: