

An approach for the physicochemical modeling of chloride ingress into cementitious materials

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1 INTRODUCTION

Chloride ion contamination is the major cause of steel corrosion in reinforced concrete structures. Chlorides may penetrate in the concrete cover from the external environment or be present in the original mix compounds. Thus, for example, chloride contamination in marine environments has resulted in significant corrosion in jetty substructures. Likewise, the use of de-icing salts has induced corrosion problems in bridge decks, and calcium chloride added as a set accelerator has caused problems to many buildings. Chloride ions, which are present in the environment, diffuse within the pores of the concrete cover. When the chloride concentration reaches a critical level at the first layer of steel rebars, depassivation of the reinforcement occurs and the corrosion process can begin, reducing thereby the structure service lifetime and affecting its stability, functionality, and aesthetics. It can be added that the decontamination of concrete from energy facilities, or the remediation of soils, is a major concern in environmental engineering. Hence, significant efforts have been made in order to understand the processes associated with chloride ingress in concrete structures exposed to aggressive environments, and to predict their service life. Chloride penetration is governed by a standard diffusion process slowed down by the binding of ions onto the solid matrix. The durability of reinforced concrete structures strongly relies upon the location of the penetration front. The propagation of the penetration front mainly depends upon two key material properties: the diffusion coefficient and the binding isotherm, the later governing the interaction between the solid and the species in solution. Although several aspects of the problem still remain to be clarified, significant process has been made in understanding the mechanisms of chloride interaction. It is well known that chloride can react with unhydrated aluminate phases to form new compounds such as Friedel's salt [1, 2]. Recent studies of Beaudoin et al. [3] and Wowra et al. [4] have also shown that chloride is able to interact with C-S-H phases. Over the years, many investigators have reported the chloride binding ability of cements and its dependence on various parameters such as the associated cation type (Ca^{2+} , Na^+), cement type and content, mineral admixtures, water-cement ratio, curing period and sulphate addition [5-6]. However, the mechanisms that result in

binding of chloride ions still not entirely clear. Depending on reaction enthalpy and mechanism, the chloride binding seems to result from both chemical reactions and physical adsorption [7]. A good knowledge of ionic ingress mechanisms in cement-based materials and implementation of the related physicochemical laws in a computer model would be necessary to evaluate properly the service-life of concrete structures.

Many research works have been devoted to the modelling of isothermal chloride ingress into concrete, from empirical to physically and chemically-based models. Within the framework of physical models, the LCPC model [8] has been developed according to a multi-species approach, which is based on the physical principles of ionic mass conservation and chemical equilibrium between a solution and the different solid phases. The diffusion of the ions is modelled by solving the Nernst-Planck/electroneutrality set of equations. The present paper aims to achieve a better understanding of the physical-chemical nature of chloride ingress. Regarding interaction ions-matrix, physical adsorption according to Langmuir's isotherm and chemical reaction are then distinguished. Furthermore, the model also accounts for the effects of dissolution/precipitation reactions on the transport mechanisms. The model considers the influence of chemically induced microstructural alterations on the transport properties of the material. The present model, consisting in the coupling of reactive and transport laws is applied to understand the chemical behaviour occurring in cement based materials due to external aggressive environment. In the first section of this paper, a brief description of the model is presented. Here, the physico-chemical mechanism of interaction ions-matrix is detailed. Finally, the model has been successfully applied to the simulation of non-steady-state diffusion test. Output data are compared with experimental results obtained on various types of concretes and conditions.

2 GOVERNING EQUATIONS OF TRANSPORT AND MASS BALANCE EQUATIONS

Within the framework of physical models, the LCPC model has been developed according to a multi-species approach, on the basis of the works reported in Marchand *et al.* [9] and Truc *et al.* [10], which include the species Cl^- , OH^- , Na^+ , K^+ , Ca^{2+} , $\text{Al}(\text{OH})_4^-$, SO_4^{2-} , along with their influence on chloride diffusion. In saturated concrete, the convection can be neglected. When sodium and chloride ions are present in solution, chlorides will diffuse faster than sodium ions, as a result of the respective chloride diffusion coefficient. Nevertheless, chlorides are charged negatively, whereas sodium ions are charged positively. An electrical field therefore takes place, which slows down the faster ions and accelerates the slower ones. As consequence, the movement of one ionic species is influenced by all the other species. Hence, the simple Fick's law is no longer appropriate and more complex models should be used. The transport of each ion i is here described by the Nernst-Planck equation, as in [11]:

$$J_i = -D_i \left[\text{grad}c_i + \frac{z_i F}{RT} c_i \text{grad}y \right] \quad (1)$$

where J_i , D_i , c_i and z_i are the flux (in $\text{mol.m}^{-2}.\text{s}^{-1}$), the effective diffusion coefficient (in m^2/s), the (“free”) concentration in the pore solution (in mol/m^3) and the valence number of each ionic species i , respectively. F is the Faraday constant ($9.64846 \times 10^4 \text{ C.mol}^{-1}$), R the ideal gas constant ($8.3143 \text{ J.mol}^{-1}.\text{K}^{-1}$), T the absolute temperature (in K) and y the local electrical potential (in V).

In equation (1), the effective diffusion coefficient D_i is defined as:

$$D_i = t f D_i^0 \quad (2)$$

where t is the tortuosity of the material and D_i^0 is the diffusion of the species i in free water, of values which can be found in physics handbooks.

On the basis of such an analysis, the set of mass balance equations for each atom present in ionic species or solid compound is as follows:

$$\frac{\partial n_i}{\partial t} + \text{div}J_i = 0 \quad (3)$$

where J_i is the flux given by Eq. (1) and n_i ($i = \text{O}, \text{H}, \text{Cl}, \text{Na}, \text{K}$, etc) denotes the total molar content of i in the ionic species or solid compounds. For example, $n_{\text{Cl}} = f c_{\text{Cl}} + 2s_{\text{Friedel's salt}} + s_{\text{Cl}}$, where f is the porosity, c_{Cl} (in mol.m^{-3}) is the chloride concentration of the aqueous phase (free chloride), $s_{\text{Friedel's salt}}$ is amount of Friedel’s salt and s_{Cl} (in mol.m^{-3} of material) denotes the amount of bound chlorides.

To complement the system of equations, another relation is needed to account for the electrical potential that is locally induced by the ion movements. Truc *et al.* [10] and Li *et al.* [12] solve the Nernst-Planck problem by using the nil current assumption. In a more general case, Marchand *et al.* [9] instead use Poisson’s equation. In this paper, the electrical interactions between ions are computed by assuming electroneutrality of the pore solution according to Nguyen *et al.* [13]:

$$\sum c_i z_i = 0 \quad (4)$$

The effect of the activity of the species in solution on ion transport, within the range of the concentrations observed in concrete, is still a subject of discussion. Some authors (e.g. Truc *et al.* [10] and Nguyen *et al.* [13]) conclude from their investigations that activity has a negligible effect, while others (e.g. Li *et al.* [12] and Samson *et al.* [16]) consider it to have a significant effect. It is assumed in following that the activity coefficients are equal to 1 primarily as the concentrations of the ions studied are not high.

3 MODELLING OF PHYSICOCHEMICAL INTERACTION IONS-MATRIX

Interactions occur between the ionic species and the solid phase. The ions may then undergo some chemical reactions with the hydrated cement

paste. For example, the penetration of chloride ions in cement-based materials may lead to the formation of chloroaluminates (Friedel's salt), while the penetration of sulphate ions is at the basis of the formation of ettringite and gypsum. Studies performed on simple cement systems clearly showed that these chemical reactions are multiionic. For instance, in addition to SO_4^{2-} , the formation of ettringite also involves Ca^{2+} , OH^- and $\text{Al}(\text{OH})_4^-$ ions. The last three ions are involved in the formation of chloroaluminates. Furthermore, the formation of ettringite, gypsum and chloroaluminates is influenced by the presence of the alkali ions Na^+ and K^+ . Some studies have also indicated that surface binding phenomena (also called physical adsorption) can have a significant influence on ionic transport mechanisms. This appears to be particularly the case for chloride penetration problems according to Beaudoin et al. [3].

Interaction ions-matrix involves complex chemical and physical process. The most usual way to describe interactions between ions in solution and the hydrated cement paste in numerical models is to use, without any exception, a simplified interaction model based on the concentration of only one ionic species. It is called the interaction isotherm, which consists in an experimental curve relating the amount of a given ion bound to solid phase as a function of its concentration in solution. In most cases, the isotherm is determined for the chloride ions. This method is used in the model based on one ion as well as in the multiionic ones. For instance, Masi et al. [14] modelled the chloride interaction with a Langmuir isotherm whereas Saetta et al. [15] modelled the same reaction with the linear isotherm. The main interest in this method lies in its simplicity. Even if it allows to model the interactions involving chloride or sulphate, in most cases it does not allow to take into account other chemical reactions occurring simultaneously like the dissolution of portlandite or the precipitation of the Friedel's salt. The use of a simple chemical model thus limits the possibility of considering some reactions that are bound to have an important effect on the ionic transport in the material. Furthermore, it blends into one unique curve the chemical reactions, where products are formed or dissolved, with the surface interactions, where ions are adsorbed onto the surface.

Hence, a more explanatory model is proposed, which is able to separate the physical and chemical chloride-matrix interaction. Even though they were presented separately, they occur simultaneously in most real life situations. The total effect on chloride binding is therefore the sum of these binding mechanisms, which are accounted for in an explicit manner in the model. It has to be underlined that most of the models found in the literature consider adsorption, but overlook the dissolution/ precipitation reactions. This is easily understandable since the latter reactions are much more complicated to model, because of the discontinuous aspect of the chemical equilibrium equation [16].

3.1 Physical adsorption:

The very high specific surface area of the C-S-H phase is often believed to substantially contribute to binding through physical adsorption. In fact, the hardened cement paste with the pore solution is an ionic solid in an aqueous solution. Such systems form an electric double layer at the interface. In electrolyte solution the surface charge is dominated by surface reactions of ionisable surface sites and electrolyte ions. For the model presented here, the physical adsorption on to the C-S-H, assumed to consist in an exchange between Cl^- and OH^- . Consider the C-S-H solid phase on which a given number of sites are available for anions. The exchange between Cl^- , OH^- and the solid phases can be written as Eq. (5):

$$\text{CSH} - \text{OH}^-_{(s)} + \text{Na}^+ + \text{Cl}^- \leftrightarrow \text{CSH} - \text{Cl}^-_{(s)} + \text{Na}^+ + \text{OH}^- \quad (5)$$

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

$$K = \frac{c_{\text{OH}^-} \cdot c_{\text{CSH-Cl}^-}}{c_{\text{Cl}^-} \cdot c_{\text{CSH-OH}^-}} = \text{const} \quad (6)$$

where, c_{Cl^-} , c_{OH^-} are chloride and hydroxyl concentrations in the pore solution (mol/m^3); $c_{\text{CSH-Cl}^-}$, $c_{\text{CSH-OH}^-}$ are the surface concentration (mol/m^2). It can be seen that, the increase in OH^- in moles occurring during chloride binding is equal to the amount of chloride ions bound in moles. Hence, the question of ionic charge imbalance in the pore solution does not arise. The amount of OH^- ions that will exchange with the Cl^- ions depends on the number of sites available for ion exchange, or indirectly the quantity of C-S-H present at any instant in the hydrated cement. Thus under this explanation, the maximum limit of ion exchange can be interpreted as the ion-exchange capacity of C-S-H. The other algebraic equation required to describe the surface reaction is given by the definition of the ion-exchange capacity N, which gives the total amount of sites available on the solid for exchanges with the aqueous phase:

$$N = c_{\text{CSH-Cl}^-} + c_{\text{CSH-OH}^-} \quad (7)$$

The combination of the two algebraic equations will give a relation of the form:

$$s_{\text{Cl}^-} = N_{\text{CSH}} S_{\text{CSH}} c_{\text{CSH-Cl}^-} = N_{\text{CSH}} \frac{S_{\text{CSH}} N K c_{\text{Cl}^-}}{c_{\text{OH}^-} + K c_{\text{Cl}^-}} = N_{\text{CSH}} \frac{a c_{\text{Cl}^-}}{c_{\text{OH}^-} + b c_{\text{Cl}^-}} \quad (8)$$

where s_{Cl^-} denotes the amount of chlorides physically bound onto C-S-H (in mol per m^3 of concrete), N_{CSH} the C-S-H content in the concrete (in mol of C-S-H per m^3 of concrete), S_{CSH} the surface area of C-S-H (in m^2/mol of C-S-H) and α , β the isotherm parameters which depend only on C-S-H properties. This expression is called an exchange isotherm.

Once the isotherm is known, it is substituted in equation (3) knowing that:

$$\frac{\partial s_{\text{Cl}^-}}{\partial t} = \frac{\partial s_{\text{Cl}^-}}{\partial c_{\text{Cl}^-}} \frac{\partial c_{\text{Cl}^-}}{\partial t} + \frac{\partial s_{\text{Cl}^-}}{\partial c_{\text{OH}^-}} \frac{\partial c_{\text{OH}^-}}{\partial t} \quad (9)$$

3.2 Chemical reactions:

The second assumed mechanism contributing to binding of chlorides is the production of Friedel's salt (hydrated calcium chloroaluminate) as a

result of the dissolution of $\text{Ca}(\text{OH})_2$ and C_3A in the presence of chloride ions. Measured values of the solubility product of Friedel's salt can be used to describe this process [1].

An initial equilibrium between the pore solution and the solid is assumed and the chemical reactions are regarded as instantaneous, as the dissolution and precipitation rates are infinitely greater than that of transport of species in solution. When the material is fully saturated with water, the transport of species is mainly diffusive. Within the pore system, ion transport causes a local thermodynamical imbalance, which immediately involves successive dissolution/precipitation of solid phases, in order to reach a new thermodynamical equilibrium. The equilibrium is calculated on the basis of the chemical equilibrium relationships of dissolution/ precipitation reactions. This is called the local equilibrium hypothesis. Under this hypothesis, the chemical equilibrium relationships are valid.

In this model, the chemical reactions considered are of the dissolution/precipitation type. The chemical equilibrium of the various solid phases present in the material is satisfied unless the solid phase has totally disappeared. The chemical equilibrium of the various solid phases present in the material is verified at each node of the mesh by considering the concentration of all ionic species at this location. Consider for example, the case of portlandite, its equilibrium constant is given by:

$$K_p = \{\text{Ca}^{2+}\}\{\text{OH}^-\}^2 \quad (10)$$

where the curly brackets {...} indicate chemical activity. Knowing that the activity is equal to $g_i c_i$ and to calculate the chemical activity coefficients g_i , several models are available. However, well-known models such as Debye-Huckel or Davies are unable to cope with the specific case of cement-based materials, which bears a highly charged pore solution. A modification of Davies's relationship was found to yield good results [17]:

$$\ln g_i = -\frac{Az_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + \frac{(0.2 - 4.17 \times 10^{-5} I) Az_i^2 I}{\sqrt{1000}} \quad (11)$$

where I (mol.m^{-3}) is the ionic strength of the solution while A and B are temperature dependent parameters. The parameter a_i varies with the ionic species i . More information on this approach can be found in Ref. [17].

For the dissolution/ precipitation process, the solid phase concentration does not appear in Eq. (10). Furthermore, when there is no solid, the product of the activity can be lower than K . So it is more precise to express it as an inequality:

$$\left. \begin{aligned} \{\text{Ca}^{2+}\}\{\text{OH}^-\}^2 &= K_p \text{ if the precipitate is present} \\ &< K_p \text{ if there is no precipitate} \end{aligned} \right\} \quad (12)$$

The inequality allows the precipitate concentration to be discontinuous in the material [18]. Suppose the usual ions (Ca^{2+} , OH^- , Na^+ and Cl^-) are initially in equilibrium with a material containing the solid $\text{Ca}(\text{OH})_2$ and allowed to leach out of the porous network. Initially, the concentration of

Ca^{2+} and OH^- obeys the relationship Eq. (10) since the solid phase is present. At the surface of the material, the product activity 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, in this case moving in the direction opposite to leaching of the ions.

The mass conservation equations will be affected by the discontinuous behaviour of this type of chemical reaction. For instance, in the zone where the precipitate concentration is zero, the unknowns are only the concentrations of ions in the aqueous phase. Elsewhere, precipitate is present, a term is added in the transport equation to account for the exchange between the aqueous and the solid phase. A technique has been developed here to solve this type of problem. The mathematics of this technique is described in the following paragraphs:

First, if one notes $s_{\text{Ca(OH)}_2}$ the amount of Ca(OH)_2 in the solid phase, as explained above the instantaneous dissolution of Ca(OH)_2 can thus be described by the following conditions (see Mainguy and Coussy [18]):

$$\begin{cases} s_{\text{Ca(OH)}_2} \geq 0 \\ K_p \geq \{\text{Ca}^{2+}\}\{\text{OH}^-\}^2 \\ s_{\text{Ca(OH)}_2} [K_p - \{\text{Ca}^{2+}\}\{\text{OH}^-\}^2] = 0 \end{cases} \quad (13)$$

Let us define the new continuous variables, in which the solid phase concentration and the ionic concentrations appear together:

$$\begin{cases} x_p = \left(\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{K_p} - 1 \right) + \frac{s_{\text{Ca(OH)}_2}}{s_{\text{Ca(OH)}_2}^o} \\ y_p = - \left(\frac{\{\text{Ca}^{2+}\}\{\text{OH}^-\}^2}{K_p} - 1 \right) + \frac{s_{\text{Ca(OH)}_2}}{s_{\text{Ca(OH)}_2}^o} \end{cases} \quad (14)$$

where $s_{\text{Ca(OH)}_2}^o$ is the reference value of the amount of portlandite. In light of this definition, the conditions (14) can then be rewritten as:

$$\begin{cases} x_p \geq -1 \\ y_p = |x_p| \end{cases} \quad (15)$$

By using the new variables, we can calculate the solid concentration and the product activity as a function of x_p and y_p :

$$\begin{cases} s_{\text{Ca(OH)}_2} = 0.5 s_{\text{Ca(OH)}_2}^o (x_p + y_p) \\ \{\text{Ca}^{2+}\}\{\text{OH}^-\}^2 = K_p [0.5(x_p - y_p) + 1] \end{cases} \quad (16)$$

In such a system, there are two mass balance equations for two ions OH^- and Ca^{2+} , the chemical equilibrium equation (Eq. (15)) and two last equations (Eq. (16)), a total of five equations. Correspondingly, there are five unknowns: two concentrations in aqueous phase $[\text{OH}^-]$ and $[\text{Ca}^{2+}]$,

one concentration in solid phase $s_{Ca(OH)_2}$, and two no meaning physic unknowns x_p , y_p . By using this technique, the transport and chemical reaction problems are here considered simultaneously. Thus, the times of calculation reduced significantly in comparison with the second technique. It should be noted that this approach assumes the existence of a local chemical equilibrium throughout the system. It means that the dissolution/precipitation rate of various species in solution is assumed as much faster than the transport rate. Recently, a dimensional analysis of various transport problems involving hydrated cement systems has clearly demonstrated that this assumption is correct in most practical cases [19].

3.3 Influence of microstructural changes on the material transport properties:

During the course of the ionic transport process, the chemical reactions besides binding or releasing ions while solid phases are precipitated or dissolved, will have an effect on the transport properties by affecting the porosity of the material. In fact, the dissolution of some phases will locally increase the porosity in the material, thus allowing the ions to move more rapidly in a structure. On the contrary, the precipitation of some solid will reduce the section of the pores and slow the ionic movement. The effects of the chemical reactions on the ionic transport are taken into account by correcting the material transport properties as a function of the porosity in each time step.

The influence of chemical reactions on the capillary porosity of the material can be calculated as follows:

$$f = f_{init} + \sum_{i=1}^M (s_i^{init} - s_i) n_i \quad (18)$$

where M is the total number of solid phases, s_i and n_i is the amount and the molar volume of the given solid phase i , respectively and f_{init} is the initial capillary porosity.

This may affect the diffusion coefficient of the material, according to an equation presented by Bentz et al. [20]:

$$\frac{D_i}{D_i^{init}} = \frac{f}{f_{init}} \left[\frac{0.001 + 0.07f^2 + 1.8H(f - 0.18)(f - 0.18)^2}{0.001 + 0.07f_{init}^2 + 1.8H(f_{init}^2 - 0.18)(f_{init}^2 - 0.18)^2} \right] \quad (19)$$

Where D_i^{init} is the initial diffusion coefficient of ionic species i and H is the Heaviside function such that $H(x) = 1$ for $x > 0$ and $H(x) = 0$ for $x \leq 0$.

4 NUMERICAL RESOLUTION

To solve such a complex system of non-linear equations (Eq. (1) to Eq. (4)), a numerical algorithm has to be used. A mass conservation equation is considered for each ionic species. This mass conservation equation includes the terms to account for ionic adsorption and for the ionic exchange between the solution and the solid (chemical reactions). The finite elements method could be used for solving such as system of equations as reported in [21]. However, the spatial discretization of this coupled system is well performed here through the finite volume method,

since the discrete form of the mass balance laws (Eq. (2)) strictly satisfied. At each step, the mass balance equations, the precipitation/dissolution equilibrium law and electroneutrality of pore solution constitute whole system of equation. The transport and chemical reaction problems are here considered simultaneously. In every time step, effective diffusion coefficients are re-evaluated in relation of the porosity, due to dissolutions and precipitations in the solid phases. The unknown variables in the adopted discretization scheme are a concentration for each ionic species taken into account and the electrical potential. An implicit approximation of the normal derivative ensuring the best stability of the scheme is used. The nonlinear set of equations is solved with a standard Newton algorithm [22]. The output comprises ionic concentration profiles, solid phase profiles and electrical potential profile.

5 APPLICATION OF THE MODELLING TO THE CHLORIDE DIFFUSION TEST

In this application, four solid components ($\text{Ca}(\text{OH})_2$, chlorides adsorbed onto C-S-H, $\text{C}_3\text{A}_{\text{eq}}$ and Friedel's salt) and seven diffusion species (OH^- , H_3O^+ , Na^+ , K^+ , Ca^{2+} , $\text{Al}(\text{OH})_4^-$ and Cl^-) are taken into account to model the dissolution/ precipitation phenomena.

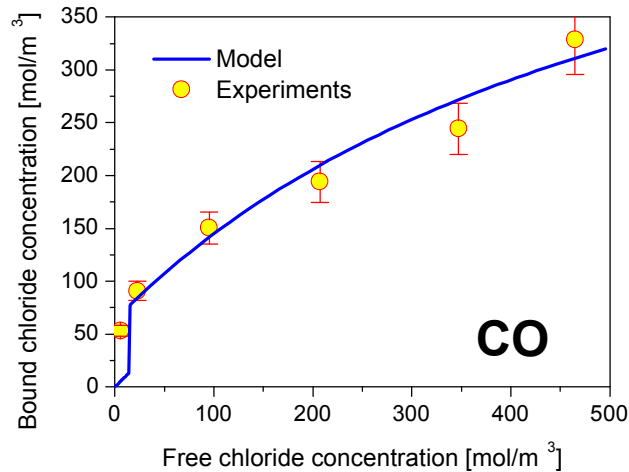


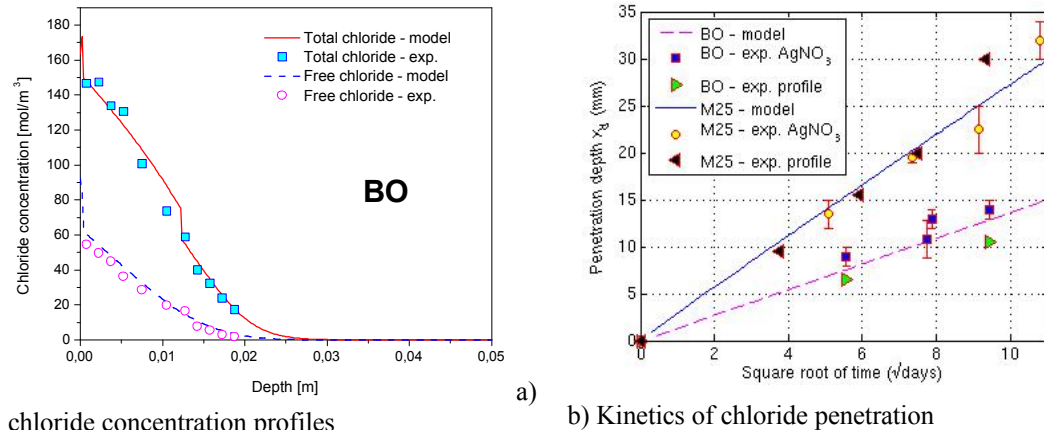
Figure 4. Chloride binding isotherm obtained on the cement paste W/C=0.35

Here, the two parameters α and β of the adsorption isotherm are assumed to depend only on C-S-H properties that are constant for all concrete mixtures prepared with the same type of cement. It is therefore possible to identify these parameters from one concrete mixture and to keep the same values to predict the behaviour of other mixtures, whatever the exposure time. α and β have been identified from the immersion test result obtained on a hardened cement paste CO (W/C = 0.35). Immersion test consists in immersing crushed samples into basic solution (NaOH: 1 g/L, KOH: 4.65 g/L) with various NaCl concentrations and at the end of the immersion period, the chloride concentration of the solution is measured [23]. The amount of bound chlorides is given as a function of the

equilibrium free chloride concentration. Part of this curve serves to identify material independent parameters that characterize the adsorbed chloride onto the CSH (these fitting parameters may depend on the nature of CSH). To complete the modelling of this curve we need additional material dependent parameters that are the initial mole content in C_3A and portlandite. These parameters can be evaluated with the help of an hydration model of cement without the need to fit them.

In fact, the value of α and β are calibrated so that the experimental isotherm curve determined with immersion test, coincide with one predicted par the model (see Fig. 4). We find $\alpha = 0.12$ and $\beta=2.26$.

The model has been applied to non-steady-state diffusion test carried out in LCPC condition with concrete BO [24]. Fig. 5 shows the predicted chloride concentration profiles. A good agreement with the experimental profiles (see [24, 25]) is displayed in Fig. 5a. The predicted penetration depth vs. square root of time (kinetics) associated to the detection threshold of $AgNO_3$ spray-test (0.3 and 0.15 per 100 g of cement, for M25 and BO respectively [25]) are compared in Fig. 5b to experimental results ($AgNO_3$ spray-tests and concentration profiles [25]). A good agreement is highlighted.



chloride concentration profiles

b) Kinetics of chloride penetration

Figure 5. Measurements (non-steady-state diffusion test in laboratory) and numerical simulations performed with the proposed model

As can be seen in the Fig. 5, there are sudden changes of slope near the surface and in the middle of the profiles of total chlorides that correspond to the locally increase the porosity near the surface of material and to the precipitation front of the Friedel's salt, respectively.

As the examples of validation, we have simulated the non-steady-state diffusion test on two other concretes M25 and M50 [24]. The cement is the same as the one used for the cement paste. The free and total chloride profiles experimentally obtained from dry-grinding of the sample and chemical analysis by potentiometric titration of the fine powder specimens are compared with the calculated profiles on Fig. 6. We note a good agreement.

It should be emphasized that the predictions yielded by the model are solely based on the mathematical equations previously described, and

that no fitting parameters are included in the model. In that respect, the good correlation between the predicted values and the experimental results further confirms the validity of the numerical model.

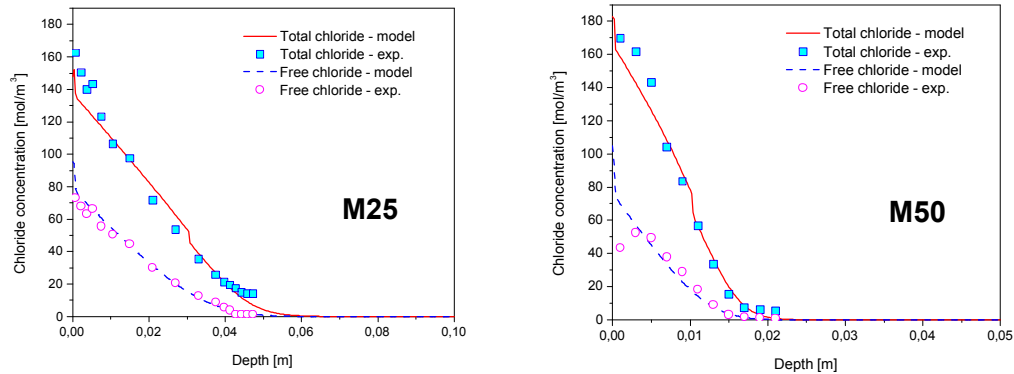


Figure 6. Chloride concentration profiles. Measurements and numerical simulations

6 CONCLUSIONS

The main objective of the modeling is to reproduce with a general approach, based on thermodynamics, the phenomena involved during the chemical external aggression of cement-based materials. The model allows the study of the influence of the matrix chemical composition, particularly the aluminates content of the cement on chloride ingress into concrete. In particular, it makes possible to take benefit of the “chemical effect” of the material, in addition to the physical barrier effect, to optimize the mix-design and to reach a given “potential” durability. In this outline binding of chlorides were treated in a very explicit manner. However, the important underlying phenomenon of chloride binding is supposed to be caused by Friedel’s salt formation in, for example, a $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4\text{-CaCl}_2\text{-H}_2\text{O}$ system. A nature extension is, therefore, to consider both other forms than Friedel’s salt formation and other systems or even combination of them. To date this approach is not fully developed and many issues must be studied further. It is, however believed that such models have to be used, since the properties governing the chloride binding and penetration are dependent on the condition on the pore solution and on solid phases.

The simulations reported in this paper point out that chloride penetration in concrete can be predicted “a priori” if the proper parameters are correctly estimated. On the basis of a limited number of input data, the model can be used to treat various practical problems. The model has been successfully applied here to the simulation of non-steady-state diffusion test. Engineers can use these numerical resolutions as a predictive tool for the estimation of the service life of reinforced concrete structures from the design stage, thus reducing costly on-site experimentation. It could also help to choose the proper concrete mixture for a given the environment to which it is exposed.

7 REFERENCES

- [1] Birnin-Yauri, U.A., Glasser, F.P., 'Friedel's salt: Its solid solution and their role in chloride binding', *Cem. Concr. Res.* **28** (1998) 1713-1723.
- [2] Suryavanshi, A.K, Scantlebury, J.D. and Lyon, S.B, 'Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate', *Cem. Concr. Res.* **26** (1996) 717-727.
- [3] Beaudoin, J.J., Ramachandran, V.S. and Feldman, R.F, 'Interaction of chloride and C-S-H', *Cem. Concr. Res.* **20** (1990) 875-883.
- [4] Wowra, O., Setzer, M.J., 'Sorpton of chlorides on hydrated cements and C₃S pastes', Proc. of Int. RILEM Workshop 'Resistance of concrete to freezing and thawing', Essen, **34** (1997) 146-153.
- [5] Tang, L., Nilsson, L.O., 'Chloride binding capacity and binding isotherms of OPC pastes and mortar', *Cem. Concr. Res.*, **23** (1993), pp. 247-253.
- [6] Delagrave, A., Machand, J., Ollivier, J.P., Julien, S., Hazrati, K., 'Chloride binding capacity of various hydrated cement paste systems', *Adv. Cem.Bas. Mat.* **6** (1997) 28-35.
- [7] Francy, O., 'Modélisation de la pénétration des ions chlorures dans les mortiers partiellement saturé en eau', PhD thesis, Génie civil, Paul Sabatier, Toulouse, 1998 (in French).
- [8] Nguyen, T.Q., Baroghel-Bouny, V., Dangla, P., Belin, P., 'Multi-level modelling of chloride ingress into saturated concrete', Proc. of Int. RILEM Workshop 'Performance based evaluation and indicator for concrete durability', Mar., 2006, Madrid, Spain.
- [9] Marchand, J., Samson, E., Maltais, Y., Lee, R.J., Sahu, S., 'Predicting the performance of concrete structures exposed to chemically aggressive environment – Field validation', *Mat. & Struc.* **35** (2002) 623-631.
- [10] Truc, O., Ollivier, J.P., Nilsson, L.O., 'Multi-species transport in saturated cement-based materials', Proc. of the 2nd RILEM Workshop "Testing and modelling chloride ingress concrete", Sep., Paris, France 1995 (Ed. By C. Andrade & J. Kropp, RILEM Publ., 2000), 247-259.
- [11] Samson, E., Marchand, J., Beaudoin, J.J., 'Describing ion diffusion mechanism in cement-based materials using the homogenization technique', *Cem. Concr. Res.*, **29** (1999), pp. 1341-1345.
- [12] Li, L.Y., Page, C.L., 'Modelling of electrochemical chloride extraction from concrete: Influence of ionic activity coefficient', *Com. Mat. Sci.* **9** (1998) 303-308.
- [13] Nguyen, T.Q., Baroghel-Bouny, V., Dangla, P., Belin, P., 'Numerical modelling of chloride ingress into saturated concrete', 2nd International RILEM Symposium on Advances in Concrete through Science and Engineering, Sep., 2006, Quebec City, Canada.
- [14] Masi, M., Colella, D., Radaelli, C., Bertolini, C., 'Simulation of chloride penetration in cement-based materials', *Cem. Concr. Res.* **27** (1997) 1591-1601.
- [15] Saetta, A.V., Scotta, R.V., Vitaliani, R.V., 'Analysis of chloride diffusion into partially saturated concrete', *ACI Mater J.* **5** (1993) 441-451.
- [16] Samson, E., Marchand, J., Beaudoin, J.J., 'Modelling the influence of chemical reactions on the mechanism of ionic transport in porous materials', *Cem. Concr. Res.*, **30** (2000), pp. 1895-1902.
- [17] Samson, E., Lemaire, G., Marchand, J., Beaudoin, J.J., 'Modelling chemical activity effects in strong ionic solution', *Comp. Mat. Sci.* **15** (1999) 285-294.
- [18] Mainguy, M., Coussy, O., 'Propagation fronts during calcium leaching and chloride penetration', *Eng. Mech.* **126** (2000) 250-257.
- [19] Barbarulo, R., Marchand, J., Snyder, K.A. and Prené, S., 'Dimensional analysis of ionic transport problems in hydrated cement systems – Part 1: Theoretical considerations', *Cem. Concr. Res.* **30** (2000) 1955-1960.

- [20] Bentz, D.P., Garboczi, E.J., Lagergren, E.S, 'Multi-scale microstructural modelling of concrete diffusivity: Identification of significant variables', *Cem. Concr. Aggre.* **20** (1998) 129-139.
- [21] Samson, E., Marchand, J., 'Numerical solution of the extended Nernst-Planck model', *J. Colloid Interface Sci.* **215** (1999) 1-8.
- [22] Eymard, R., Gallouet, T., Herbin, R., in: P. Ciarlet, J.L. Lions (Eds.), Handbook of numerical Analysis. The Finite Volume Method, in press.
- [23] Chaussadent, T., Baroghel-Bouny, V., Care, S., Perrin, B., Bonnet, S., François, R., Francy, O., 'Transferts dans les bétons et durabilité des ouvrages. Analyse des interactions physico-chimiques entre les chlorures et le béton', Rapport de synthèse LCPC/LETHEM/LMDC, (2000), 41 p.
- [24] Baroghel-Bouny, V., 'Which toolkit for durability evaluation as regards chloride ingress into concrete? : Part II. Development of a performance approach based on durability indicators and monitoring parameters', Proc. of the 3rd Int. RILEM Workshop 'Testing and modelling chloride ingress into concrete', Sept., 2002, Madrid, Spain (Ed. By C. Andrade & J. Kropp, RILEM Publ., 2004), 137-163.
- [25] Baroghel-Bouny, V., Belin, P., Castellote, M., Rafai, N., Rougeau, P., Yssorche-Cubaynes, M.P., 'Which toolkit for durability evaluation as regards chloride ingress into concrete ? Part I: Comparison between various methods for assessing the chloride diffusion coefficient of concrete in saturated conditions', Proc. of the 3rd Int. RILEM Workshop, Sept., 2002, Madrid, Spain (Ed. By C. Andrade & J. Kropp, RILEM Publ., Bagnaux, 2004), PRO 38, 105-136.