A numerical model including thermodynamic equilibrium, kinetic control and surface complexation in order to explain cation type effect on chloride binding capability of concrete

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HIGHLIGHTS

- A reactive transport model with reaction kinetics and surface complexation is proposed.
- Chloride binding capability of CEM II exposed to chloride solutions is studied.
- Chloride binding capability decreases with cation type: $Ca^{2+} > Mg^{2+} > Na^+ = K^+$.
- The higher the pH is, the lower the chloride is absorbed on C-S-H.
- Sulfates reduce chloride binding capability because of sulfate absorption on C-S-H.

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ABSTRACT

The impact of cation type, sulphate and pH on chloride binding is studied using a numerical model combining thermodynamic equilibrium, kinetics and surface complexation. First, the model is validated by comparing numerical and experimental results obtained on a CEM II concrete material exposed to *NaCl*, *KCl*, *MgCl*$_2$ and *CaCl*$_2$ solutions. Then, the numerical results are discussed to improve our understanding of the differences in chloride binding capability generally observed in the literature. A strong coupling between cation, pH and sulfate affecting chloride binding is highlighted. After six months of exposure, chloride binding due to Kuzel's salt formation has little effect on chloride binding capability whatever the chloride salt solution. The results also confirm the existence of a relationship between pH and chloride binding capability previously observed experimentally in the literature. When some sulfate ions are present in the chloride solution, they reduce the chloride binding capability because of the sulfate absorption process on C-S-H.

1. Introduction

Chloride diffusion is one of the major cause of reinforcement corrosion in concrete exposed to seawater or de-icing salts. Many authors consider that corrosion initiation stage of steel reinforcement in concrete depends on the chloride threshold value which can be expressed in a number of different ways, such as: total chloride content in relation to the weight of cement (or concrete) [1], free chloride contents [2], $[Cl^-]/[OH^-]$ [3,4]. To predict the chloride concentration threshold value in cementitious materials, the performance-based approach Fib model code [5] requires the consideration of the empirical chloride binding isotherm. In this model, based on the analytical solution of the Fick's second law, the chloride binding isotherm is therefore one of the most significant input data of the Fib model code.

A survey of the literature reveals that a considerable amount of effort has been devoted in the last decade to the study of chloride binding in cementitious materials. Page et al. [6], for instance, show that the OH^- concentration (or pH) arising from the external environment significantly affects chloride binding. Tritthart [7] and Sandberg et al. [8] both experimentally demonstrate that lower pH values give higher chloride ions binding, which may be accounted for by a competition among OH^- and Cl^- ions for the sorption sites of hydrated cement [7]. Moreover, Roberts [9] and Zhu et al. [10] consider that an increase in pore solution pH enhances the

solubility of chloroaluminate salt (Friedel's salt, Kuzel's salt) consequently reducing chloride binding due to chloroaluminate salt formation.

Furthermore, Arya et al. [11], Page et al. [6], Delagrave et al. [12], Zhu et al. [10], DeWeerdt et al. [13] and Song et al. [14] experimentally observe that cations associated to chloride salts affect chloride binding capability. These authors note that the maximum chloride binding capability is reached when the cementitious materials are exposed to a $CaCl_2$ solution. In a more detailed manner, Zhu et al. [10] and Song et al. [14] experimentally describe that the binding capability of chloride decreases in the order $Ca^{2+} > Mg^{2+} > Na^+ \approx K^+$ when the cementitious samples are exposed to $CaCl_2, MgCl_2, NaCl$ and KCl solutions, respectively. Wowra et al. [15] find that the Ca^{2+} cations sorption onto C-S-H surfaces increases the positive charge and in turn the chloride binding in the double electrical layer. Moreover, according to Delagrave et al. [12], the nature of the associated cation significantly affects chloroaluminate solubility and accessibility of chloride ions to sorption sites. On the basis of experimental results, Yuan et al. [16] suggest that, in the presence of Na^+, cementitous materials have higher pH value than with Ca^{2+} and Mg^{2+}. Zhu et al. [10] demonstrate that Na^+ and K^+ may increase the pH value of pore solutions. These arguments imply that pore solution pH affects chloride binding capability.

However, DeWeerdt et al. [13] experimentally prove that the relationship between the decrease in pore solution pH and the increase in chloride binding for exposure solutions like $MgCl_2$ or $CaCl_2$ is not valid when the SO_4^{2-} ions concentration is significant. Byfors [17] and Wowra et al. [15] have previously shown that an increase in sulfate ion concentration causes a sharp decrease in chloride binding capability. DeWeerdt et al. [13] suggest that one reason might be the chloride sorption process onto C-S-H and the chloride binding due to the chloroaluminate salt formation capacity. C-S-H indeed, when exposed to $MgSO4$ and $MgCl_2$, fixes more SO_4^{2-} ions than Cl^- ions, leading to the decreased chloride sorption onto C-S-H. The SO_4^{2-} ions react with the AFm phase to precipitate ettringite which is more stable than the chloroaluminate salts (Friedel's salt, Kuzel's salt) and as a result chloride binding due to chloroaluminate salt formation decreases.

The experimental studies mentioned above emphasize the coupling effect of three different factors affecting chloride binding capability: cation of chloride salt, solution pH and sulfate concentration. It is, however, interesting to verify and confirm the arguments proposed through a numerical investigation. The numerical study presented in this paper is carried out through the development of a numerical model, its validation through the comparison with the experimental results found in the literature and the analysis of the chloride binding mechanism in a final section.

A number of chloride transport models are found in the literature: some models based on Fick's second law or on the multispecies ionic transport equations [18–20], or physically and chemically coupled model [21]. These models use global binding isotherms to determine the total chloride amounts as a function of the free chloride amounts. However, isotherms parameters must be calibrated on the basis of experimental data [19].

Numerical models must describe simultaneously chloride sorption and binding due to the chloroaluminate salt formation. Chloride sorption can be described using a surface complexation model considering the surface charge and the double electrical layer. Chloride binding due to the chloroaluminate salt formation is described by chloroaluminate precipitation/dissolution using thermodynamic equilibrium and kinetic control. The aim of this paper is to investigate the factors affecting chloride binding in concretes exposed to chloride and other ions. A reactive transport model including thermodynamic equilibrium, kinetic control and surface complexation modelling that has been previously described for chloride ingress and external sulphate attack [22,23] is used.

First, the governing equations used to simulate the reactive transport model in saturated cementitious materials are presented: transport equations, surface complexation describing interaction on mineral surfaces, principle of thermodynamic equilibrium and kinetic laws. Then, the model input data of the model are discussed: parameters of solid species under kinetic constraints, surface complexation parameters, original mineralogical composition of hydrated cement, exposure conditions and numerical procedure, sorption reaction in thermodynamic database. Finally, the modelled results are compared with some experimental data from the literature to validate the numerical model.

2. Reactive transport modeling and input data

In this section the reactive transport modeling is exposed on several aspects, such as reactive transport equations, thermodynamic and complexation formation constants and kinetics of dissolution/precipitation. However, the description of the model is intentionally reduced since it has been previously published and described in details for chloride transport in concrete [23] and external sulphate attack [22].

2.1. Reactive transport equations

The coupling of chemistry and transport in porous media was used to describe the mineral phases evolution in time and space. Toughreact, which is based on integral finite differences method, has been developed for this purpose by solving chemically reactive nonisothermal flows of multiphase fuids in porous media [24]. A sequential iterative operator-splitting method is operated to solve the system.

In saturated condition without convection phenomena the main mechanism considered is diffusion which is coupled to chemistry according to the following equation:

$$\frac{\partial \phi C_j}{\partial t} = D_e \nabla(\nabla C_j) + q_j \tag{1}$$

where D_e is the effective diffusion coefficient of species j (m^2.s^{-1}) which value is the same for all species, ϕ the porosity and C_j the molar concentration of free species j in a pore solution (mol.m^{-3} of solution). q_j is a source or sink term (mol.m^{-3}.s^{-1}) that denotes the removing or releasing species j and that is evaluated by chemical calculations. In this study, q_j combines sorption onto C-S-H surface (see paragraph 2.4), mineral dissolution/precipitation as explained in paragraphs 2.2 and 2.3 and aqueous complexation in solution.

Porosity can evolve with time by actualizing volume of each mineral species [25] that can precipitate or dissolve. Effective diffusion coefficient can also evolve, as follows:

$$D_e^{n+1} = \frac{\phi^{n+1}}{\phi^n} D_e^n$$

where n labels the number of the time step.

2.2. Thermodynamic formation constants

The thermodynamic formation constants of species are taken from CEMDATA07 and Nagra/PSI TDB thermodynamic databases [26]. The thermodynamic data are exposed in Table 1. C-S-H is supposed to be a mix of tobermorite ($CaO/SiO_2 = 0.83$) and jennite