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A COMSOL-PHREEQC interface for modeling the multi-species transport of saturated cement-based materials

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HIGHLIGHTS

- A COMSOL-PHREEQC interface is developed to model the multi-species transport.
- The interface is based on the physiochemical essential processes of the transport.
- The interface is verified by the two published experiments.

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ABSTRACT

A COMSOL-PHREEQC interface based on MATLAB language is developed to simulate a multi-dimensional and multi-species ionic transport for cement-based materials. This interface couples the physical and chemical interactions between pore solution and cement hydrates (PHREEQC) into the Nernst-Planck equations (COMSOL) using a sequential non-iterative approach (SNIA). Based on the thermodynamic insight, the phase-equilibrium model and the surface complexation model are used to express the physical and chemical interactions. In addition, the influence of the variation of the porosity on the ionic transport is considered. Moreover, two reported experiments are taken as an example to illustrate the application of the interface and to verify its accuracy. The results indicate that the developed interface can accurately predict the transport of chloride in cement-based materials.

1. Introduction

The chloride-induced corrosion of reinforcing steel has been recognized as one of the most primary factors in degrading the durability of reinforced concrete (RC) structures, especially in the coastal or deicing salt environment [1,2]. When the amount of chloride adjacent to the reinforcing steel reaches to the threshold value, the passive layer of reinforcing steel is destroyed, and then the corrosion initiates at the case of the presence of oxygen and water.

Generally, due to diffusion, capillary suction, advection, electrical migration, etc., chloride ions are driven to penetrate into cement-based materials from environment [3]. Therefore, many numerical models have been developed to investigate the ionic transport of cement-based materials in the past few decades [3–17]. Liu et al. proposed a multi-phase and multi-component ionic transport model of cement-based materials [8–11,18,19], and the Langmuir or linear binding isotherm of chloride ion was used to consider the interactions between ionic species and cement hydrates. Zhang et al. used a lattice Boltzmann method to model the ionic diffusivity in cement-based materials [13], but they neglected the physical or chemical interactions between ionic species and cement hydrates. Shi et al. [20] used a multi-ionic model to describe the chloride transport in concrete, and both a depth-dependent ionic diffusion coefficient and the Freundlich binding isotherm of chloride ion were adopted in their model. Essentially, chloride binding in cement-based materials is a result of the physical and chemical interactions between pore solution and cement hydrates [21–25], and it plays a prominent role on

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Nomenclature

K_p	thermodynamic equilibrium constant
c_i	concentration of the ion i in the pore solution (mol/L)
γ_i	activity coefficient of the ion i
R	universal gas constant (8.314 J/(K·mol))
T	absolute temperature (K)
μ	ionic strength of the solution (mol/L)
z_i	charge of the ion i
σ	surface charge density of C-S-H (C/m^2)
F	faraday constant (96,485 C/mol)
S	specific surface area (m^2/g)
M	concentration of C-S-H in cement hydrate (g/l)
Γ_H	densities of bound protons (mol/m^2)
Γ_{OH}	densities of bound hydroxyl ions (mol/m^2)
Γ_C	densities of bound cations (mol/m^2)
Γ_A	densities of bound anions (mol/m^2)
c	molar electrolyte concentration
$c_{DL,i}$	concentration of the ion i in the diffuse layer
ψ_0	surface potential of C-S-H (V)
J_i	flux of the ion i ($mol/m^2/s$)
ψ	Electrical potential (V)
D_{i_free}	diffusion coefficient of the ion i in free water (m^2/s)
D_{i_p}	pore solution diffusion coefficient of the ion i (m^2/s)
τ	tortuosity of pore structure
γ	constrictivity of pore structure
ρ_0	initial porosity
ρ	porosity at the time t
$f(\rho)$	effect of the variation of the porosity on the pore solution diffusion coefficient
m_p	molar mass of the hydrate phase p
θ_p	density of the hydrate phase p
n_p	amount of substance of the hydrate phase p at the time t
n_{p0}	initial amount of substance of the hydrate phase p
D_{Cl_R}	chloride migration coefficient
R_i	source term determined by the thermodynamic interactions

the transport process [26]. Therefore, Samson et al. coupled the chemical reactions into a multi-species ionic transport model to describe the degradation of the cement-based materials exposed to an aggressive environment [14,15]. Johannesson et al. considered the chemical reactions between pore solution and cement hydrates by adopting ion exchange reactions in the developed multi-species ionic diffusion model of concrete [16]. Hosokawa et al. further developed the multi-species transport model that adopted the ionic binding of C-S-H and the precipitation and dissolution of cement hydrates [17]. Elakneswaran et al. integrated the phase-equilibrium model, the surface complexation model and the multicomponent diffusion model to simulate the multi-species transport of cement-based materials using PHREEQC code [3]. These models greatly promote the development of the multi-species transport model in cement-based materials based on the essence of physical and chemical reactions during the transport process, but they [3,14–17] are limited to one dimensional numerical model.

It is of significance to develop a multi-dimensional and multi-species transport model of cement-based materials based on the physical and chemical essential processes of the transport. Therefore, this paper develop an effective interface that couples the physical and chemical interactions between pore solution and cement hydrates (PHREEQC) into Nernst-Planck equations (COMSOL), achieving a multi-dimensional and multi-species reactive-transport simulation in cement-based materials.

2. Theoretical model

2.1. Thermodynamic model of the physical and chemical interactions between pore solution and cement hydrates

Based on the thermodynamic insight, the phase-equilibrium model of the dissolution and precipitation reactions, and the surface complexation model of the double electrical layer are used to describe the physical and chemical interactions between pore solution and cement hydrates. The phase-equilibrium reactions between cement hydrates and free ions in pore solution are expressed by the law of mass action (LAM) equations [21], which can calculate the amount of each hydrate phase that can react reversibly with pore solution when achieving the equilibrium [3].

$$K_p = \prod_i (\gamma_i c_i)^{n_{i,p}}, \tag{1}$$

where K_p denotes the thermodynamic equilibrium constant of the pure phase p in the cement hydrate; γ_i and c_i denote the activity coefficient and the concentration of the ion i, respectively; $n_{i,p}$ denotes the stoichiometric coefficient of the ion i participating in the dissolution and precipitation reactions. K_p can be calculated by the following equation [3]:

$$K_p = \exp\left(-\frac{\Delta_r G_T^0}{RT}\right), \tag{2}$$

where R is the universal gas constant (8.314 J/(K·mol)) and $\Delta_r G_T{}^0$ is the standard Gibbs energy of reaction at the temperature T. Cemdata2007 [27,28] gives K_p and $\Delta_r G_T{}^0$ for nearly all the phases of cement hydrate. The dissolution and precipitation reactions are considered, shown in Table 1, and the equilibrium constants are given in Table 1. In the paper, the chloride chemical binding of cement hydrates is assumed to only produce Friedel's salt, and Kuzel's salt do not be considered.

Additionally, the activity coefficient of aqueous specie is related to the ionic strength by Davies equation,

$$\log(\gamma_i) = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{\mu}}{1 + 1.4\sqrt{\mu}} - 0.3\mu\right), \tag{3}$$

or extended Debye-Huckel activity equation,

$$\log(\gamma_i) = \frac{-Az_i^2 \cdot \sqrt{\mu}}{1 + \mathrm{B} \cdot a_i \cdot \sqrt{\mu}} + b_i \cdot \mu, \tag{4}$$

where μ is the ionic strength of aqueous solution (mol/L); z_i is the charge of the ion i; a_i and b_i are the ion-specific parameters from

Table 1
Dissolution and precipitation reactions and the equilibrium constants (K_p) about cement hydrates at 25 °C [3,27].

Phases	Formula	$\lg K_p$
CSH	$5(CaO)\cdot 3\,(SiO_2)\cdot 6.3(H_2O) + 1.7\ H_2O = 5Ca^{2+} + 3SiO(OH)_3^- + 7OH^-$	−13.1659
CH	$Ca(OH)_2 + 2H^+ = Ca^{2+} + 2H_2O$	22.79937
AFt	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O = 2Al(OH)_4^- + 6Ca^{2+} + 26H_2O + 4OH^- + 3SO_4^{2-}$	−44.9085
AFm	$Ca_4Al_2(SO_4)(OH)_{12}\cdot 6H_2O = 2Al(OH)_4^- + 4Ca^{2+} + SO_4^{2-} + 4OH^- + 6H_2O$	−29.2628
Friedel's salt	$Ca_3AlCaCl_2\cdot 10H_2O = 4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4OH^-$	74.93