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Multiphase modelling of ionic transport in cementitious materials with surface charges

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ABSTRACT

This paper presents a two-dimensional, two-phase ionic transport model with a surface charge at solid–liquid interfaces. The present model is applied to investigate the effect of surface charges at the solid–liquid interface on the ionic transport in a cement paste when it is subjected to an externally applied electric field. The surface charge in the present model is considered by modifying the Nernst–Planck equation in which the electrostatic potential is dependent not only on the externally applied electric field but also on the dissimilar diffusivity of different ionic species including the surface charges. The coupled transport equations of individual ionic species are solved numerically using a finite element method built in commercial software COMSOL. Some important features about the effect of surface charge on the concentration distribution, migration speed and flux of individual ionic species are discussed.

1. Introduction

Chloride induced corrosion of reinforcing steel in concrete has been recognized as the most critical threat to the durability of reinforced concrete structures, particularly those exposed to chloride-rich environment such as marine and offshore infrastructures [1]. It is generally acknowledged that reinforcing steel bars embedded in concrete start to depassivate when the concentration of the surrounding chloride reaches a certain threshold value [2–4]. The depassivation results in a significant corrosion rate of steel leading to cracking and spalling of the concrete cover, and eventually local failure of the structure. Therefore, it is important to understand how fast chloride ions can penetrate in the concrete, in order to predict the initial corrosion time and the service life of the structures in a given environment.

Since the early 1980s a considerable amount of laboratory and field tests have been carried out to investigate the mechanism of chloride ingress in concrete (e.g., [5–11]). These experimental methods can be classified into two categories. One is the diffusion test, in which the main driving force of the chloride penetration is the concentration gradient. The other is the migration test, in which the dominant driving force of the chloride penetration is the electrostatic potential gradient generated by the externally applied electric field. Based on the obtained experimental results, many prediction models have also been developed to examine the influence of various involved factors on the penetration of chloride ions in cementitious materials [12–26].

The diffusion and migration of ionic species in an electrolytic solution can be described by Fick's Law and Nernst–Planck equation, respectively. In the early migration models developed for cementitious materials the electrostatic potential used in the Nernst–Planck equation is merely determined by the externally applied electric field. In this case, the transport equations of individual ionic species in the material can be treated separately and solved independently [5–8,27,28]. The influence of ionic interaction between different ionic species in cementitious materials on the electrostatic potential was considered first by Yu and Page [29], then Li and Page [15,16], and followed by others [24,30–36], in which the electrostatic potential is determined based on not only the externally applied electric field but also the internal electrostatic potential generated by the dissimilar diffusivity of different ionic species. Consequently, the transport equations of individual ionic species in the material are coupled each other and have to be solved dependently. Recently, the multicomponent transport model has been expanded from a single phase to two- and three-phases to consider the heterogeneous nature of the cementitious materials [20,37,38–40].

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Notations

C_k	concentration of k-th ionic species (mol/m^3)	x	coordinate in horizontal axis (m)
C_s	surface charge at solid-liquid interfaces (mol/m^3)	y	coordinate in vertical axis (m)
D_k	diffusion coefficient of k-th ionic species (m^2/s)	z_k	valence number of k-th ionic species
F	Faraday constant (C/mol)	z_s	valence number of surface charge
J_k	flux of k-th ionic species (mol/(m^2 s))	ε_o	permittivity of a vacuum (C/(V m))
N	total number of ionic species in solution	ε_r	relative permittivity of water
R	universal gas constant (J/(mol K))	Φ	electrostatic potential (V)
t	time (s)		
T	absolute temperature (K)		

Despite the aforementioned numerous studies, there has been little work on the effect of the electrical double layer (EDL) on the ionic transport in cementitious materials. The EDL is a well-known electrochemical phenomenon, which can be found at the interface of the solid hydrates surface and the electrolytic pore solution in cementitious materials [41]. Due to the mixed mechanisms such as ionization, ionic adsorption and ionic dissolution, the cement hydrates will develop a surface charge when brought into contact with the pore solution [36]. The charge imbalance near the surface will create a local electric potential difference. Ions in the pore solution of opposite charge to that of the surface (counterions) are attracted towards the charged surface, while ions of like charge (coions) are repelled from the surface due to the electric force. However, of finite size, the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically absorbed, which creates an inner layer called 'stern layer'. Beyond the stern layer to the unaffected pore solution, the electric attraction and repulsion is combined by the mixing tendency resulting from the random thermal motion of the ions. These ions are then distributed in a 'diffuse' manner and this layer is called 'diffuse layer'. The stern layer and diffuse layer form the structure of EDL [42]. The local electric charge and potential imbalance in the EDL have a great impact on ionic transport in porous media, especially in fine pores [43,44]. Therefore, the surface charge on the pore surface is another important factor that should be taken into account in the ionic transport in concrete.

In the past decade, much effort has been made to investigate the surface charge of various cement hydrate phases. Due to lack of direct test methods, most studies determined the sign and the amount of the surface charge by measuring the zeta potential, which is the potential at the shear surface between the stern and diffuse layers and is closely related to the surface charge. Many researchers conducted zeta potential measurement on synthetic C–S–H suspensions [45–47], which are the main hydration products of cement-based materials. They found that the surface of C–S–H gel is negatively charged at low concentrations of Ca^{2+} in solution with a negative zeta potential. However, the zeta potential becomes positive when the concentration of Ca^{2+} is higher than a certain value. Elakneswaran et al. [48,49] studied the surface potential characteristics of different major mineral phases of hydrated cement paste. It was reported that Friedel's salt and portlandite have positive surface charge while others show negative surface charge in water. Overall, the hydrated cement paste shows positive net surface charge by dissociation and adsorption. Nevertheless, the experiment results and theory of the surface charge are still not strong enough to make a general conclusion about the sign and the magnitude of the surface charge in cementitious materials.

Typically, the ionic and electric potential distributions in the EDL can be estimated by a linearized version of the Poisson–Boltzmann equation, which is only applicable at low potentials. With a constant electric potential boundary condition, one can get the results of electric potential distribution perpendicular to the charged surface, which is called the *Debye-Hückel* approximation. Then the ionic concentration distribution can be calculated by using the Boltzmann equation. However, the zeta potential measurements of cementitious materials indicate that the magnitude of the surface potential is relatively high for the linearization to be applicable [42]. Arnold et al. [50] presented a numerical solution of the full nonlinear Poisson–Boltzmann equations and examined the implications of EDL on the ionic diffusion in discrete pore geometries. The scheme is more applicable than the analytical *Debye-Hückel* approximation in cementitious materials. Friedmann et al. [51] developed an analytical solution of the Poisson–Boltzmann equation by replacing the Poisson equation with the electroneutrality approximation. They demonstrated that the overlapping of two diffuse layers in gel pores strongly influence the EDL effect on ionic transport. Nguyen and Amiri [52] investigated the EDL effect on chloride penetration in unsaturated concrete by solving the multi-species ionic transport equations coupled with that of humidity. The EDL effect is introduced by modifying the ionic concentration with influencing parameters, which are mainly dependent on the zeta potential and the pore diameter. Their numerical results showed that the EDL effect reduces in unsaturated concrete due to the discontinuity of liquid phase, but increases in the concrete containing slag when compared to that with fly ash due to the high ionic strength of pore solution caused by the ferrous ions of slag.

In this paper, a two-dimensional numerical model is developed to simulate the transport of multiple species in a cement paste with surface charges. The model is used to simulate the ionic transport taking place in a cement paste when it is subjected to a rapid chloride migration (RCM) test. The numerical results show that there is an interaction between the local electric field generated by the surface charges and the global electric field generated by the externally applied voltage. The effect of surface charges at the pore surfaces on the ionic transport, particular the chloride penetration, in the two-dimensional model of cement paste is examined and discussed, through which the importance of using two-dimensional geometry is highlighted.

2. Two-dimensional, two-phase multicomponent ionic transport model with surface charges

It is assumed that the cement paste to be studied herein is fully saturated and there are no chemical reactions such as ionic adsorption/desorption between solid and liquid phases and ion–solvent molecules interactions in the pore solution. The transport of ionic species in the cement paste is the balance of the competing effects between the random thermal motion of the ions and the electric force, which is valid not only in the diffuse layer of EDL but also in the bulk solution where the effect of the surface charge can be ignored. The conventional Poisson–Boltzmann equation