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# Modeling of ionic diffusivity in non-saturated cement-based materials using lattice Boltzmann method

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ABSTRACT

The ionic diffusivity in non-saturated cement-based materials is quantitatively studied using lattice Boltzmann method. The Shan–Chen multi-phase lattice Boltzmann model modified by incorporating the Carnahan–Starling equation of state into the model is used to simulate the equilibrium distribution of water and gas phases with density ratio as high as 775 in the three-dimensional microstructure of cement paste at various degrees of water saturation. The lattice Boltzmann diffusion model is subsequently applied to simulate the diffusion process of the ionic species through the partially saturated cement paste. Before the application of the modified Shan–Chen model, the benchmark tests including bubble test and contact angle test are carried out to validate it. It is shown that the ionic diffusivity is greatly influenced by the degree of water saturation. The simulated relative ionic diffusivity as a function degree of water saturation is in good agreement with the experimental data obtained from literature. In addition, the effect of w/c ratio on the ionic diffusivity through cement paste under non-saturated conditions is investigated. It indicates that there is a significant difference between the relative diffusivity for cement paste with w/c ratios of 0.4 and 0.5 over the whole range of water saturation degree. However, the difference of relative diffusivity for cement paste with w/c ratios of 0.5 and 0.6 is not obvious.

## 1. Introduction

Transport properties of cement-based materials are widely studied over the last few decades, since they play a critical role in the durability assessment and design of reinforced concrete structures. It has been increasingly realized that in durability-based design the ionic diffusivity in cement-based materials is a major indicator for evaluating the ability of these materials to prevent the penetration of aggressive chemical species (e.g., chloride, sulfates, etc.) and subsequently predicting the service life of reinforced concrete structures in a marine or deicing salt environment. Owing to the alternate wetting and drying cycles by tidal and splash action, the structure is seldom saturated except in the submerged parts. Therefore, it is essential to investigate the influence of degree of water saturated upon the ionic diffusivity in cement-based materials.

In view of its importance several researches have been done in the last few years to experimentally, analytically and numerically determine the ionic diffusivity through non-saturated cement-based materials. However, it should be noted that up to now only few results have been presented. In the experimental investigation, Nielsen and Geiker [1] applied an alternative experimental procedure to obtain an initial chloride content on the surface of specimens by a temporal immersion of the specimens in a concentrated NaCl solution for 2 h followed by drying the surface with a hair drier (avoiding excessive heating) until the specimens reached a constant weight prior to chloride exposure. By curve-fitting the measured chloride content profile to the 'instant plane source' solution of Fick's second law of diffusion, and the chloride diffusivity in mortar with a water-to-cement (w/c) ratio of 0.5 at different degrees of water saturation were obtained. They found that the chloride diffusivity was significantly influenced by the moisture content. Climent et al. [2] and de Vera et al. [3] proposed an experimental setup and procedure based on an instantaneous deposition of chloride by subjecting the surface of specimens to the interaction with gaseous hydrogen chloride produced in combustion of PVC. The chloride content profiles derived from the tests at selected time intervals were adjusted to the 'instant plane source' solution of Fick's second law of diffusion according to the particular initial and boundary conditions of the experimental procedure. The authors applied this experimental test method to measure the chloride diffusivities in unsaturated concretes with controlled water contents. The obtained chloride diffusivity decreased about two orders of magnitude as the degree of water saturation declined from 80% to 30%. Guimaraes et al. [4] developed a simplified procedure based on putting solid NaCl in contact with the surface of specimens during diffusion test to estimate the chloride diffusivity through partially saturated mortars with water saturation degree from 50% to 100%. The results indicated an obvious dependence of the chloride diffusivity on the degree of water saturation. It is noticeable that the tests are usually time-consuming. It takes from several weeks to several months or longer [2]. Furthermore, it is very difficult to maintain the water saturation degree of specimens as constant during the tests [4].

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In the analytical investigation, by considering the analogy that exists between chloride and water diffusion in non-saturated concrete, Saetta et al. [5] proposed an *S*-shaped curve function to describe the chloride diffusivity at a given humidity ($D_{RH}$) relative to the chloride diffusivity at 100% RH ($D_{100\%RH}$) as the following equation

$$\frac{D_{RH}}{D_{100\%RH}} = \left(1 + \left(\frac{1-RH}{1-RH_c}\right)^4\right)^{-1}. \tag{1}$$

This equation is similar to that presented by Bazant [6] to quantify the relationship between water diffusivity and relative humidity in the simulation of water diffusion in non-saturated concrete. In Eq. (1), $RH_c$ is defined as the critical relative humidity where the chloride diffusivity is half of $D_{100\%RH}$. $RH_c$ is considered to be equal to 75% [5]. This model is actually a semi-empirical model by fitting the limited experimental data. A further validation of this model with more experiments is required before its application.

In the numerical investigation, Martys [7] studied the effect of saturation degree on the fluid diffusivity through two general types of sphere porous media, i.e. overlapping and non-overlapping sphere porous media. The phase separation of a binary mixture of wetting fluid (e.g., liquid) and non-wetting fluid (e.g., gas) was simulated by a lattice Boltzmann (LB) model. After obtaining the final location of each fluid phase in the pore space, the bulk conductivity was determined using network model. Finally, the diffusivity was calculated on the basis of Nernst–Einstein-relation which described directly the relationship between the ionic diffusivity and conductivity. It was shown that there was a significant dependence of fluid diffusivity on saturation degree. The diffusivity decreased very sharply at or around a saturation of 50%. It is worth to point out that the LB model applied in Ref. [7] is only available for the liquid–gas mixture with a density ratio of less than 58 [8]. However, with respect to water–gas system, its density ratio is approximately 1000/1.29 = 775, which is beyond the capacity of this model.

The primary purpose of this present work is to develop a numerical framework to estimate the ionic diffusivity in non-saturated cement-based materials based on the LB method. A modified multi-phase LB model is used to simulate the water–gas phase equilibration and distribution at various degree of water saturation within the pore space in the three-dimensional (3D) microstructure of cement paste. On the basis of water–gas equilibrium distribution, a new porous medium domain is derived by converting the gas-filled pores to impermeable solid-like nodes. Subsequently, the LB diffusion model is applied to simulate the ion diffusion through the new domain and calculate the corresponding effective diffusivity based on Fick's law. The simulated relative diffusivities of cement paste specimens at various degree of water saturation are computed and verified with experimental data obtained from literature. In addition, the effect of w/c ratio on the relative diffusivity of cement paste is evaluated in a quantitative manner.

## 2. Diffusion in cement-based materials

Diffusion mechanism defines the movement of the molecular species in fluids, such as liquids, gases or ions, from zones of high concentration of molecules to low concentration as a result of molecular collisions. The pure diffusion of molecular species in a fluid within the pore air space can be described by Fick's law

$$\frac{\partial C}{\partial t} = -D_0 \nabla^2 C \tag{2}$$

where the left term represents the purely diffusive flux of the molecular species, $C$ is the concentration of the molecular species in the fluid phase, $D_0$ is the intrinsic free molecular diffusion coefficient (diffusivity), $\nabla C$ is the concentration gradients of molecular species.

Neglecting the physical or chemical interactions between ionic species and the components of cement-based materials, e.g. chloride binding, diffusion in cement-based materials is generally governed by the macroscopic diffusion coefficient [7]

$$\frac{\partial}{\partial t}(CS\phi) = -D_e \nabla^2 C \tag{3}$$

where $S$ is the degree of fluid saturation, $\phi$ is the porosity of cement-based materials, $D_e$ is the macroscopic effective diffusion coefficient that varies with degree of saturation, porosity and geometry of cement-based materials.

For the saturated cement-based materials, the pore space is fully filled with water (water-saturated) or gas (gas-saturated) and provides an effective diffusion path for ions or gas, respectively. With regard to the non-saturated cement-based materials, a part of pore space is filled with water and the other part is gas-filled. Thus, the molecular species of ions and gas are limited to pass through the respective parts of pore network. The ratio of the effective diffusion coefficient of a fluid through non-saturated cement-based materials and that through saturated cement-based materials is commonly referred to as the relative diffusion coefficient $D_{rel}$. It represents the influence of degree of fluid saturation on the fluid diffusion coefficient.

## 3. Multi-phase lattice Boltzmann model

To estimate the ionic diffusivity in partially saturated cement-based materials, it is essential to simulate the multi-phase flow in cement-based materials beforehand. In LB method there are three popular types of models for multi-phase flow, i.e. the color-gradient-based model proposed by Gunstensen et al. [9], based on the immiscible lattice gas of Rothman and Keller [10], the original Shan–Chen (SC) model derived by Shan and Chen [11,12] and the free-energy (FE) model proposed by Swift et al. [13]. All these models have been employed in numerical studies of flow problems and each of them has its distinct advantages. A review and evaluation of these models can be found in Refs. [14,15]. Among these multi-phase LB models, the SC model is widely used due to its simplicity, ease of implementation and remarkable versatility. It can easily handle fluid phases with different densities, viscosities and wettabilities. The major drawbacks of the original SC model are that it is not well-established thermodynamically and the maximum liquid–gas ratio is limited to 58 [14]. These disadvantages can be overcome by incorporating different kinds of equations of state (EOS) into the original SC model [8]. Furthermore, the wettability with various contact angles of the liquid/gas to the solid surface can be conveniently implemented by changing a parameter named the virtual density of wall [16]. The SC model has been successfully applied to study the multi-phase flow through general two-dimensional porous media by several researchers [14,16,17]. According to their findings, the results are in good agreement with the theoretical or experimental data. Therefore, SC model is chosen to simulate the multi-phase flow in cement-based materials in this study.

### *3.1. Modification of the Shan–Chen model*

At the microscopic level, a fluid made up of particles (the fluid molecules) can move in all directions as a result of collisions of particles with other particles. The probability of these particles' position in the physical space is dynamically described by the continuous Boltzmann equation. The LB method approximates the continuous Boltzmann equation by discretizing the physical space into a set of uniformly spaced lattice nodes and the velocity space into a finite set of microscopic velocity vectors. The discrete velocity vectors are defined for the propagation of fluid molecules. The microscopic movement of particles at each lattice node is represented by the particle distribution functions which are defined as the probability of finding a particle around the