LATTICE BOLTZMANN SIMULATION OF THE IONIC DIFFUSIVITY IN UNSATURATED CEMENT PASTE

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Abstract

In order to assess the durability of concrete structures, it is essential to investigate the ionic diffusivity under unsaturated conditions. Simulation of the ioinc diffusivity in unsaturated cement-based materials is big challenge due to the complicated microstructures and the difficulties in modelling of multi-phase fluid flow in cement-based materials. In this study, the 3D microstructure of cement paste is obtained from X-ray μCT with a high resolution. In the simulation, the Shan-Chen multi-phase lattice Boltzmann model is modified to simulate the equilibrium distribution of water and gas in the obtained 3D microstructure at various degree of water saturation. A lattice Boltzmann diffusion model is applied to simulate the ionic diffusion and determine the ionic diffusivity based on Fick's law. It was found that the ionic diffusivity shows a strong dependence on the degree of water saturation. The simulated results fit very well with the experimental data obtained from literature.

1. INTRODUCTION

The penetration of aggressive chemical species such as chloride and sulfates is one of the major problems that impact the durability of reinforced concrete structures, especially for the structures in marine or deicing salt environment. There are three types of mechanisms for the penetration of aggressive ions into concrete corresponding to different driving forces, among which diffusion of ions is the primary one. Under a certain condition, the rate of ionic diffusion through concrete is strongly dependent on the ionic diffusion coefficient also called diffusivity which is considered as a major index for prediction of service life and assessment of durability of reinforced concrete structures. The ionic diffusivity in concrete may be affected by many factors, such as, chemical composite, water-to-cement (w/c) ratio, curing age and environmental conditions (e.g., humidity, temperature). The former factors have been

taken into account in previous work presented in [1] and [2]. The influence of degree of water saturation (directly relates to the humidity) on the ionic diffusivity in cement-based materials is studied.

In the past few decades, a number of attempts have been made to study the ionic diffusivity in unsaturated cement-based materials by both of experimental test and numerical simulation. With respect to the experiments, until recently some test procedures have been propoosed due to the difficulty of maintaining a certain degree of water saturation during the test. Nielsen and Geiker [3] developed an alternative experimental procedure to measure the chloride profile in mortar at two different degrees of water saturation of 53.8% and 59.4%. They determined the corresponding chloride diffusivities by fitting the derived chloride profile to the 'instant plane source' solution of Fick's second law of non-steady state diffusion. Climent et al. [4] proposed an experimental setup and procedure based on an instantaneous deposition of chloride to obtain the chloride content profiles which are subjected to the habitual error-function solution of Fick's second law of diffusion to estimate the chloride diffusivity in unsaturated concrete. With respect to numerical simulation, Martys [5] applied a lattice Boltzmann model to study the phase separation of a binary mixture of wetting fluid and non-wetting fluid in the partially saturated overlapping and non-overlapping spherical porous media respectively, the results of which were regarded as inputs to determine the bulk conductivity using a network model. Finally, the ionic diffusivity was calculated according to Nernst-Einstein-relation which describes directly the relationship between the ionic diffusivity and conductivity. The wetting and non-wetting fluid referred in [5] do not involve the water-gas system, the density ratio of which is very high about 1000/1.29 = 775 at 20 ℃ due to the limitation of the used lattice Boltzmann model.

The main objective of this work is to estimate the ionic diffusivity in unsaturated cement paste by using lattice Boltzmann (LB) method. A multi-phase LB model modified from Shan-Chen model is applied to simulate the equilibration and distribution of water and gas in the pore network at various degree of water saturation. The three-dimensional microstructure used in this study was derived from the X-ray computed micro-tomography (CT). With the equilibrium distribution of water and gas, the LB diffusion model as described in [2] is utilized to simulate the ionic diffusion in the new domain and determine the ionic diffusivity. The simulated diffusivity in cement paste with various degree of water saturated are compared with the experimental data obtained from literature.

2. METHODOLOGY

At microscopic level, a fluid made up of particles (the fluid molecules) can move randomly 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 with regular lattice nodes and setting the velocity space as microscopic velocity vectors. The microscopic movements of particles at each lattice node are represented by the particle distribution functions. The evolution of particle distribution functions satisfies the following LB equation [6]

$$f_i\left(x + e_i \delta t, t + \delta t\right) = f_i\left(x,t\right) - \frac{1}{\tau}\left[f_i\left(x,t\right) - f_i^{eq}\left(x,t\right)\right] \tag{1}$$

where f_i and f_i^{eq} are the non-equilibrium and equilibrium particle distribution function at

location x at time t, τ is the relaxation time which is related to the kinematic viscosity of fluid as $v=c_s^2(\tau-0.5)$ with $c_s^2=1/3(\delta x/\delta t)^2$, herein, the lattice-spacing δx and time-step δt are defined as 1 lu and 1 ts (lu, ts and mu refer to lattice units, time step and mass units respectively in the LB method), e_i is the microscopic velocity at location x at time t. The subscript i represents the number of allowed velocity directions on the lattice. In this study, we use a very popular D3Q19 model (as shown in Fig. 1), which is a three-dimensional model with nineteen microscopic velocity vectors e_i (i=0, 1, … ,18) as listed Eq. (2).

$$e_i = \begin{bmatrix} 0 & 1 & -1 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 & 0 & 0 & -1 & -1 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 0 & 1 & -1 & 0 & 0 & 1 & 1 & 1 & -1 & 0 & 0 & -1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 1 & -1 & 1 & -1 & 0 & 0 & 1 & -1 & 1 & -1 \end{bmatrix} \quad (2)$$
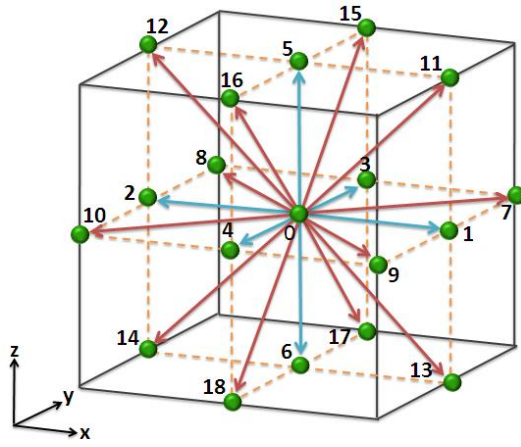

Figure 1: Lattice velocity direction of the D3Q19 model

For the D3Q19 model, the equilibrium distribution function f_i^{eq} is given by

$$f_i^{eq} = w_i \rho \left[1 + \frac{e_i \cdot u}{c_s^2} + \frac{(e_i \cdot u)^2}{2c_s^4} - \frac{u \cdot u}{2c_s^2} \right] \quad (3)$$

where ρ and u are the macroscopic density and velocity respectively, w_i is the weight factor associated with i^{th} direction which is given as w_i=1/3 (i=0), w_i=1/18 (i=1, 2, … ,6) and w_i= 1/36 (i=7, 8, … ,18).

In terms of the multi-phase LB model, Shan-Chen (SC) single component multi-phase model [7, 8] is one of the most used models for the simulation of multi-phase fluid flow (e.g., liquid and gas) in porous media. In the SC LB model, the macroscopic local density (mass) $\rho(x, t)$ and velocity $u(x, t)$ of each lattice node are related to the distribution function $f_i(x, t)$ and the force item consisting of fluid-fluid interaction force F_{int}, fluid-solid adhesion force F_{ads} and external force F_g including gravity effects by

$$\rho = \sum_{i=0}^{n} f_i \quad (4)$$

$$u = \frac{1}{\rho} \sum_{i=0}^{n} (f_i \cdot e_i) + \frac{\tau \cdot (F_{\text{int}} + F_{ads} + F_g)}{\rho} \quad (5)$$

Microscopically, the separation between two phases is the result of fluid-fluid interaction

force. In the SC model, the fluid-fluid interaction force F_{int} between the fluid particles at lattice location x and its nearest neighbor nodes at time step t is given by

$$F_{\text{int}} = -G\psi(x,t)\sum_{i=1}^{18} w_i\psi(x+e_i,t)e_i \qquad (6)$$

where G is the coefficient of the attractive forces between fluid particles which represents the intensity of the interparticle interaction, ψ is the so-called "effective mass" which is a function of local density ρ. The value of G is negative for attraction and positive for repulsion between particles. Increasing G within the critical value will lead to a tendency towards phase separation and a sharper interface. The "effective mass" function ψ directly relates to the interaction force. The forms of ψ control the detailed nature of the interaction potential and determine the equation of state (EOS) of the fluid system [7]. The function ψ can be chosen arbitrarily in the SC model but should be monotonic and bounded. By choosing the function ψ properly, the essential feature of the liquid-gas phase transition will be exhibited. A particular form of the function ψ was proposed by Shan and Chen in their original paper [7]

$$\psi(\rho) = \rho_0\left(1 - \exp(-\rho/\rho_0)\right) \qquad (7)$$

where ρ_0 is constant which is generally set to 1.

The EOS describes the relationship between temperature, pressure and volume (or density) for a given fluid or a mixture consisting of many forms of phases such as liquid and vapor phases of water. In the SC model, the form of fluid-fluid interparticle interaction force described by Eq. (7) leads to the EOS of the system expressed as [9]

$$p = c_s^2\rho + \frac{c_s^2 g}{2}\psi(\rho)^2 \qquad (9)$$

If there is no fluid-fluid interaction force, the fluid will act as an ideal gas. Otherwise, the EOS is dependent on the form of "effective mass" function ψ. By choosing different forms of ψ, one can obtain different EOSs. Besides SC EOS, the other typical EOSs are van de Waals, Redlich-Kwong (R-K), Redlich-Kwong Soave (R-KS), Peng-Robinson (P-R) and Carnahan-Starling (C-S) equations. They can be incorporated into SC model by transforming Eq. (9) into

$$\psi(\rho) = \sqrt{\frac{2\left(p - c_s^2\rho\right)}{c_s^2 g}} \qquad (10)$$

In this study, to solve the limitation of the original SC model and achieve a high density ratio (e.g., water-gas system in cement-based materials), the SC model is modified by incorporating the C-S EOS into the model which is given as

$$p = \rho R_0 T \frac{1 + b\rho/4 + (b\rho/4)^2 - (b\rho/4)^3}{(1 - b\rho/4)^3} - a\rho^2 \qquad (11)$$

with $a = 0.4963 R_0^2 T_c^2 / p_c$, $b = 0.18727 R_0^2 T_c / p_c$. In simulations, a, b and R_0 are generally set to 1, 4 and 1 respectively [9].

The adhesion force between liquid/gas phase and solid phase in the SC model F_{ads} is given by [8]

$$F_{ads} = -G\psi(x,t)\sum_{i=1}^{18} w_i\psi(\rho_w)s(x+e_i)e_i \qquad (12)$$

where ρ_w represents the virtual density of the solid phase which is a free parameter applied to denote different wettability, $s(x+e_i)$ is an indicator function which is set to 1 if the site $(x+e_i)$ is a solid node and to 0 otherwise. The adhesion force emerges once the neighboring node of a fluid node is solid. By varying the value of ρ_w, the different contact angle between fluid and solid surface can be conveniently obtained.

3.   THREE-DIMENSIONAL MICROSTRUCTURE

The three-dimensional microstructure used in the LB simulation is acquired by X-ray computed micro-tomography (CT). The experimental procedure, micro-tomography image processing and analysis were described in [10]. The used Portlant cement is ASTM type I. The w/c ratio of the specimen is 0.5. The resolution of micro-tomography images is about 0.485 μm/voxel. Figure 2 shows the three-dimensional microstructure and its pore structure of the representative elementary volume (REV) of cement paste at curing age of 120 days which was extracted from a cylinder region of interest (ROI) with a diameter of 250 μm and thickness of 100 μm. The REV size was selected as $100 \times 100 \times 100$ μm^3.
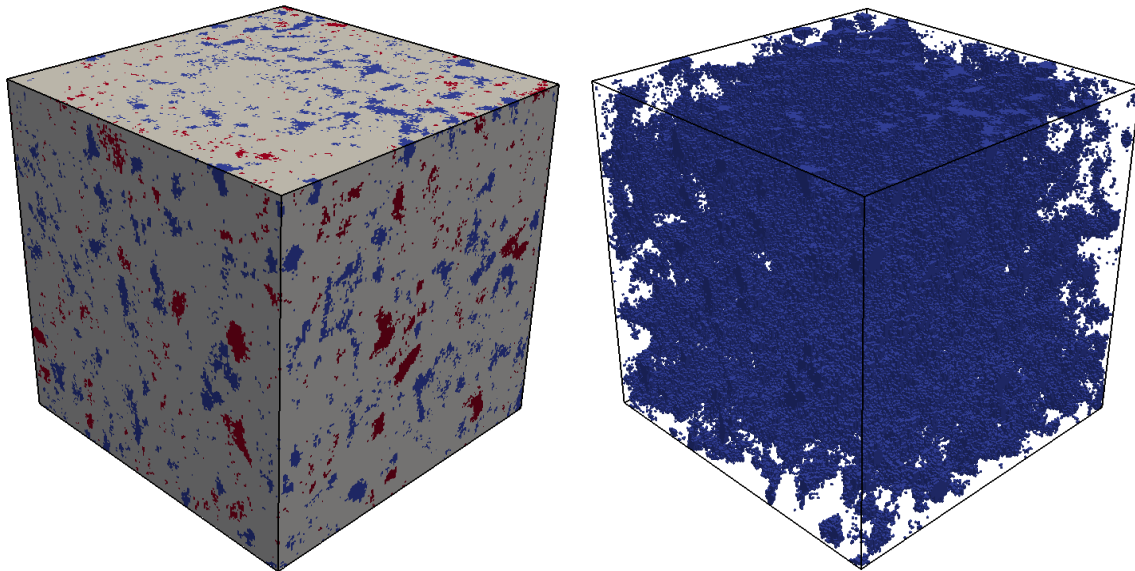

Figure 2: The microstructure and its pore structure of the REV of cement paste at curing age of 120 days (red region represents anhydrous cement grains, light grey region is hydration product and blue region is capillary pore)

4.   RESULTS AND DISCUSSION

4.1 Equilibrium distribution of water and gas

The modified SC multi-phase LB model is used to establish the equilibrium distribution of water and gas phase in cement paste. Initially, the water and gas phase are randomly placed in the pores so that a desired degree of water saturation can be obtained. The LB simulation is run until the equilibrium state is achieved. Figure 3 illustrates the equilibrium distribution of water and gas in the microstructure and pore structure of cement paste (as shown in Figure 2) with a degree of water saturation of 64.5%. The red region is the solid phase consisting of

anhydrous cement grains and hydration products. The blue region represents the water phase and the light grey region is the gas phase. It can be observed that water phase tends to cover the solid surface and fill the pores with smaller size. On the contrary, the gas phase tends to occupy the central parts of larger pores which strongly affect the ionic diffusion through the domain. In this case, pores filled with water form an interconnected pore network for ions passing through. However, the gas-filled pores seem to be isolated which means that there is no effective pathway for gas (for instance oxygen or carbon dioxide) to diffuse. When the degree of water saturation decreases, water will typically forms a thin film on the solid surface. In this case, the number of porous channels with a continuity of pore solution will greatly decrease and the ionic diffusion pathway will be significantly lengthened. As a consequence, the ionic diffusion process is greatly restricted and the ionic diffusivity will obviously reduce. In contrast, the number of pores occupied by gas phase gradually increases and they will eventually form a percolating network through the pore structure. When the equilibrium arrangement of water and gas phase in the pore structure is achieved, the gas-filled pores are converted into solid-like nodes which are considered to be non-diffusive like solid phase in cement paste. Thus, a new domain consisting of pore nodes saturated with water phase, solid-like nodes and solid nodes is created.
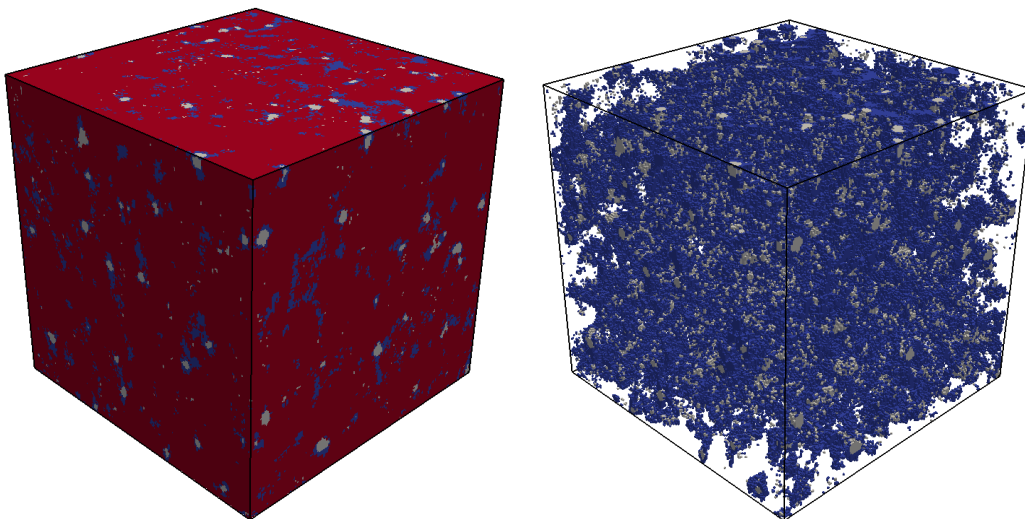

Figure 3: Equilibrium distribution of water and gas phase in the microstructure and its pore structure of cement paste with a degree of water saturation 64.5% (red region is solid phase, blue region represents water phase and light grey region is gas phase)

4.2 Relative diffusivity

The simulation of the ionic diffusion through the new domain is performed using the LB model for diffusion as introduced in [2]. In the simulation, the ion concentration on the inlet and outlet surfaces is set to 1 and 0 respectively. Thus, a concentration gradient of 1 is achieved. The effective ionic diffusivity through the new domain can be estimated according to Fick's first law once the steady-state condition is reached. The ratio of the effective ionic diffusivity in the new domain relative to that in initially saturated situation is defined as the relative diffusivity. Figure 4 shows the relative diffusivity as a function of water saturation

degree. It is clearly seen that the relative diffusivity is significantly affected by the degree of water saturation. The relative diffusivity reduces steadily with the decrease of water saturation degree. The effective diffusivity turns to zero while the degree of water saturation is approximately 44% which means that there is no continuous pathway for the ions to diffuse any more. At this moment, the degree of water saturation is defined as the critical saturation S_c. The relations between the relative diffusivity D_r and water saturation degree (WSD) is fitted to a quadratic polynomial equation given by Eq. (13). The correlation coefficient is 0.998 which indicates that Eq. (13) fits the simulated results very well.

$$D_r = -0.00005 \cdot WSD^2 - 0.024 \cdot WSD - 0.987 \tag{13}$$

The experimental data from [3] are also plotted in Figure 4 for the purpose of comparison. In their experiment, a mortar with w/c ratio 0.5 was used. The estimated effective chloride diffusivity in the mortar specimens for degree of water saturation at 53.8%, 59.4% and 100% are 5.5×10^{-12}, 7.9×10^{-12} and 20.2×10^{-12} m^2/s respectively. Thus, the corresponding relative diffusivity at degree of water saturation 53.8% and 59.4% is 0.209 and 0.295 respectively. It can be observed that the simulated relative diffusivity shows an a very good agreement with the experimental data. It is worth to point out that although the specimens in their experiment are mortar, whereas, the samples in the LB simulation in this study are cement paste. Nevertheless, the good agreement between experiments and simulation give firmly support to the suitability of simulation in this study to estimate the ionic diffusivity through partial water saturation cement-based materials.
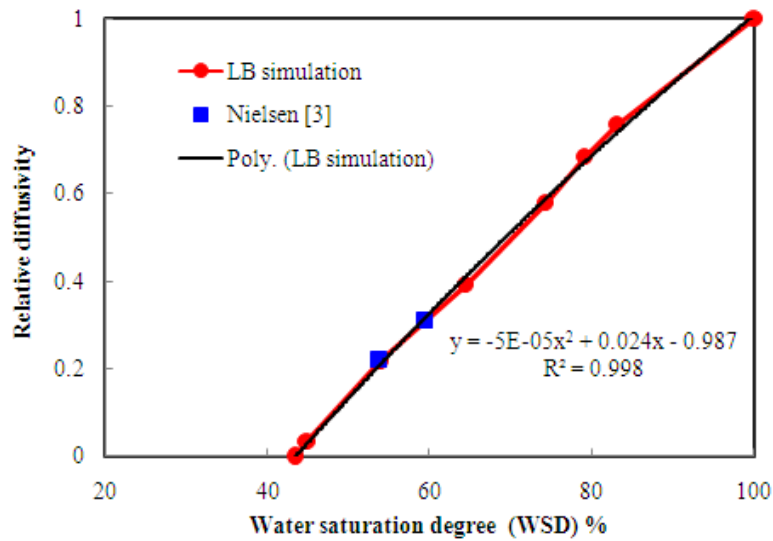

Figure 4: Relative diffusivity as a function of water saturation degree

5.   CONCLUSIONS

This paper was dedicated to study the ionic diffusivity in cement paste with various degree of water saturation by using lattice Boltzmann method. From present study, several major conclusions can be drawn as follows:

- Water phase prefers to fill the pores with small size, covers the solid surface and forms a thin layer. On the contrary, the gas phase tends to occupy the central parts of large pores and restrains the diffusion of ions.
- The ionic diffusivity is significantly affected by the degree of water saturation. The ionic diffusivity reduces steadily with the decrease of degree of water saturation. The relation between the relative diffusivity and degree of water saturation follows a quadratic polynomial equation.
- There exists a critical water saturation at which the capillary pores occupied by water phase are not interconnected any more. For cement paste with w/c ratio of 0.5 at curing age of 120 days generated from X-ray µCT, the critical water saturation was 44%.
- The simulated data are in excellent agreement with the experimental data obtained from literature.

ACKNOWLEDGEMENTS

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