Microstructure-Based Modeling for Water Permeability of Hydrating Cement Paste

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Abstract

Water permeability is a key property for the serviceability and durability of concrete structures, which governs the transport of fluid through the pore network in the cementitious material. A microstructure-based numerical test method is proposed and employed to predict the permeability of hydrating cement paste. Numerical samples characterizing the evolution of the microstructure of cement paste are generated using the computational code HYMOSTRUC3D. Based on the three-dimensional (3D) finite element method (FEM), the pore-scale flow of water induced by pressure-gradient through the sample is simulated and the corresponding permeability is estimated. Water flow characteristics in the hydrating cement paste and the evolution of the permeability against different water-to-cement ratio (w/c), porosity, curing age and degree of hydration are investigated by numerical simulations. The simulated results are verified in comparison with available theoretical solutions, experimental data and numerical predictions obtained from the literature. Due to the dilution and tortuosity effects, the permeability decreases with the increase of cement hydration and the decrease of w/c. The connectivity of the pore throat plays an important role in affecting water movement in hydrating cement paste. The developed modeling approach is capable to investigate the transport properties of cement paste, which may provide basic parameters for multiscale modeling of concrete performance and strongly support the coupled multiphysics analysis in concrete engineering.

1. Introduction

The estimation of durability and service life of concrete structures is a theoretical and technological issue of great concern in material science and civil engineering (Hall and Hoff 2012; Mehta and Monteiro 2013; Wang and Bao 2017). Most deterioration of durable concrete owing to freeze-thaw cycles, carbonization and corrosion chemistry, is related to the intrusion of water or water-soluble agents (e.g. sulphates and chlorides). Water permeability is of great practical significance to investigate the water-related deterioration processes of cement-based materials (Reinhardt 1997; Chen 2019). Water penetration into cementitious material depends largely on its micropore structure, which is the most important factor dominating the transport properties of cement paste (Bittnar 2006; Picandet et al. 2011; Zalzale and McDonald 2012). Because of the disordered and complicated pore structure of cement paste, the permeability anisotropy at the microscopic level has a major influence on the macrosopic performance of concrete structure (Bittnar 2006). Therefore, it is essential to investigate the water movement behavior within the micropore space and to estimate the permeability of cement paste for advancing the state of the art in durability assessment and service life prediction in engineering practice.

Intensive research efforts have been undertaken to directly measure the permeability of hardened cement paste for many years (Reinhardt 1997; Picandet et al. 2011; Hall and Hoff 2012; Mehta and Monteiro 2013). Indirect approaches have also been developed to assess the impacts of microscale composition on moisture transport properties. For instance, the permeability of cement paste has been estimated through the theoretical analysis like Katz-Thompson equation or GEM theory based on the porosity and pore characteristics deriving from novel detecting techniques inclusive mercury intrusion porosimetry (MIP) (Cui and Cahyadi 2001), scanning electron microscope (SEM) (Liu et al. 2018), non-contact impedance measurement (NCIM) (Tang et al. 2014), transmission X-ray microscope (TXM) (Sun et al. 2014), backscattered electron mode (BSE) (Labri et al. 2016), nuclear magnetic resonance (NMR) (Huang et al. 2016; Zhang et al. 2018) etc. Recently, Liu et al. (2018) analyzed the characteristic of microstructure using the SEM technique and established the relationship between the permeability based on the GEM theory and pore structure characteristics using the MIP test results. Tang et al. (2014) utilized the NCIM to quantify the pore structure in cement paste and proposed a fractal permeability model to evaluate the permeability evolution based on the measured results from NCIM. Sun et al. (2014) adopted the TXM technique to detect the micro-

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structure and then the Katz-Thompson equation was adopted to compute the permeability. However, the permeability of cement paste is still difficult to be measured by physical experiment, especially for the modern cementitious material with high strength, low porosity and low permeability, which would raise difficulties in obtaining adequate side surface sealing and applying sufficiently high pressure to the specimens (Zalzale and McDonald 2012; Li et al. 2016b). Experimental measurements would be time-consuming and costly, and furthermore there is a considerable variation in the measured data. Since the number of tested specimens is relatively small and usually limited in a physical experiment, it may be not sufficient to satisfactorily capture the microstructural characteristics and monitor moisture movement in micropores for cementitious materials.

Attempting to overcome these limitations, numerical methods focusing on microstructural models with random microstructure instead of actual microstructures straightforwardly derived from the experimental observation (e.g. electron microscope images) are developed to perform structural characterization and property prediction for hydrating cement paste. By introducing the concept of “numerical concrete”, the internal microstructure of hydrating cement paste is simulated based on the computer-based cement hydration models, for instance, HYMOISTRUC3D by TU Delft (van Breugel 1995), CEMHYD3D by NIST (Bentz 1997) and μC by EPFL (Bishnoi and Scrivener 2009). Subsequently, numerical modeling approaches are widely employed to establish the link between the cement hydration microstructure (affected by w/c, curing age and porosity) and material properties (e.g., permeability and elastic modulus). Several numerical methods have sought to predict the permeability evolution of cement paste during the hydration process, among which the most commonly utilized one is Lattice Boltzmann method (LBM). Recently, Zalzale and McDonald (2012) investigated the permeability of cement paste using LBM and concluded that the simulated permeability is larger than the experimental data, while LB results obtained from μC compare favorably with other numerical methods, like CEMHYD3D. Zhang (2017) presented a LB modeling approach for estimating permeability of cementitious material, where the 3D microstructure was constructed based on the X-ray micro-CT. It is seen that the simulated results achieve a good agreement with experimental data and indicate that the moisture distribution and permeability of cement paste are strongly dependent on its microstructure. Banala and Kumar (2017) investigated the influence of the compositions (e.g., liquid-to-solid ratio, degree of hydration and filler content) on water permeability of plain and blended cement paste based on the LBM. The simulations were verified against experimental data and numerical results published in the literature. Besides, other numerical methods are being developed to estimate the permeability of cement paste including discrete element method (DEM) (Li et al. 2016a, 2017a), finite difference method (FDM) (Sun et al. 2014), tube network (Ye et al. 2006; Koster et al. 2006) and fractal model (Yu et al. 2018a).

A majority of these investigations, particularly LBM, are performed based on the lattice voxels for the numerical modeling. Such an assumption of the geometrical configuration may experience difficulty in ensuring the computational convergence (inclusive boundary condition setup and calculation singularity problem) and might underestimate the actual permeability because of the regular assembly of voxels adopted in the lattice construction (Mazaheripour et al. 2018).

As the most common numerical method, the finite element method (FEM) possesses the advantages of flexibility and ability in dealing with complex geometries and boundary conditions. It has also been utilized in microstructure-based modeling of cement paste during the hydration process for predicting properties such as elastic moduli (Bitnar 2006; Gao et al. 2018) and compressive strength (Hlobil et al. 2016). Furthermore, this method is simple and convenient for coupled multiphysics simulation (moisture transport, heat transfer, deformation and damage evolution) and multiscale structural analysis (micro, meso and macro levels) (Xu et al. 2017; Chen 2019), which has received more and more attention in recent years for concrete degradation modeling. However, studies on water permeability of hydrating cement paste using 3D FEM are rarely reported. This may partially be attributed to the fact that the microstructure-based FE modeling will require intensive computation to solve basic equations of stiffness (Tian and Bian 2013; Gao et al. 2018). It will be interesting to develop a FEM modeling scheme for investigating the water permeability of cement paste with heterogeneous microstructure, to put forward the coupled multiphysics simulation and multiscale structural analysis.

In this paper, a microstructure-based numerical test method based on 3D FEM is proposed and employed to describe the pore-scale flow in the microstructure and compute the permeability of hydrating cement paste. The multi-phase microstructure of the cement paste composite is generated by a 3D computational model (i.e., HYMOISTRUC3D), which has been reported previously to study the effects of various factors on the evolution of the microstructure of cement-based systems (van Breugel 1995; Zalzale and McDonald 2012; Zhang et al. 2013). Based on the Navier-Stokes equations, the pore-scale flow within the internal structure of hydrating cement paste is simulated and the permeability against w/c ratio, porosity, curing age and degree of hydration is predicted. To verify the accuracy of the proposed numerical test, benchmark simulations of simple geometries are conducted. The evolution of microstructure of cement paste and its effect on the water transport characteristics, and the corresponding permeability are investigated.
2. Microstructure modeling of cement paste

The material properties of hydrating cement paste are strongly related to its microstructural composition (Zheng et al. 2010; Zhang et al. 2013; Larbi et al. 2016). Cement paste is a highly heterogeneous material composed of the anhydrous cement grains, the hydrates and the pores, as plotted in Fig. 1 obtained from the literature (Larbi et al. 2016). Presently, the tested specimens utilized in experimental measurement are usually so limited that it is still difficult to exhibit the overall internal geometry of the microscale composite structure. In response to this situation, numerical hydration model is an alternative way to interpret the hydration process of cement paste and characterize its microstructure.

With the development of computer, hardware and numerical methodology, computer-based cement hydration models are being used to carry out critical investigations on the evolution of the pore structure and the transport properties during cement hydration process. Hydration model can be categorized into spherical-based and pixel-based models represented by HYMOSTRUC3D and CEMHYD3D, respectively. The applicability and features of the two models and others, such as, Jennings-Johnson model, HydratICA, μIC, THAMES, Durability models of concrete such as DuCOM and IPKM, are discussed in detail and summarized in the literature (Dolado and van Breugel 2011; Thomas et al. 2011; Ouzia and Scrivener 2019; Zhou et al. 2019).

In this present study, the HYMOSTRUC3D computational code is adopted for characterizing the microstructure of cement paste during hydration process. For this hydration model, cement paste is assumed as four-phase composite material consisting of unhydrated cement, inner product (C-S-H with high density), outer product (C-S-H with low density) and capillary pores (van Breugel 1995; Zhang et al. 2013). A well-known Rosin-Rammler particle size function is employed to describe the size distribution of cement particle, given by,

$$G(D) = 1 - \exp(-bD^n)$$  (1)

where $D$ represents the diameter of cement particle (m), $G(D)$ denotes the mass percentage passing the sieve with diameter of $D$. $b$ and $n$ are constants. According to the mechanism of cement hydration, the radius of unhydrated cement particle is written as,

$$\Delta \delta_{v, j+1} = K_0(\theta) \cdot \Omega(\tau) \cdot \Omega(\delta_j) \cdot F_j(\cdot \delta_j)^\alpha \cdot \Delta \Delta$$  (2)

where $\Delta \delta_{v, j+1}$ represents the increase of the penetration depth at time step $\Delta \tau$ (m), $K_0$ is the basic rate factor and $\delta_j(\cdot)$ denotes the transition thickness (m). $\Omega$ and $F_j$ are the influence factors of water and temperature on hydration process. Detailed description of this hydration model could be referred to in the work of van Breugel (1995).

To describe the process of hydration, the degree of hydration, $\alpha$, is defined by,

$$\alpha = \frac{V_{\text{hydrated}}}{V_{\text{cement}}}$$  (3)

in which $V_{\text{hydrated}}$ and $V_{\text{cement}}$ denote the volume of hydrated cement and original cement (m³), respectively.

Typical numerical samples generated by the microscopic hydration model are given to display the microstructure of hydrating cement systems in Figs. 2 and 3, where the main constituents of portland cement CEM I 42.5 N are completely identical with the that reported in the literature (Zhang et al. 2013). 3D cement hydration structure of three numerical samples with different w/c at curing age of 7 d is illustrated in Fig. 2. With the reduc-
tion of w/c, the hydrated products (i.e., green and red phases) grow to fill a higher volume of pore space and meanwhile the connectivity of the pores (i.e., blue phase) decreases which could give rise to alter the permeability. Figure 3 demonstrates the hydration process in the central profile of the samples with w/c = 0.4 at different hydration degrees and curing ages. The distribution of pore structure is complicated and irregular, which may be not appropriate to postulate these pores as cylindrical. Such is contrary to the assumption of cylindrical pores in MIP test. It is clearly revealed that the hydration of cement proceeds rapidly in a very complex manner with the increase of curing age. As a result, the suspended cement particles (i.e., grey phase) continuously react and dissolve, and more hydration products appear and settle toward the surface of the cement particles. The hydration products gradually connect with each other accompanying with the pores distributing unevenly and pore connectivity reducing largely. Meanwhile, the strength of hardened cement paste develops and the permeability decreases. Concerning the mechanism of cement hydration, hydration products coating around the unhydrated cement particles could prevent the intrusion of water, the hydration rate slows down and the cement paste changes from suspended solids initially to porous media gradually. Furthermore, it is indicated that pore throat openings (i.e., diameter of accessible pores through which water could penetrate to reach internal pores) become finer versus curing age due to cementation of hydration products. Pore throats are visualized as irregular structures, which is a critical link for water intrusion into the pore network of cementitious materials.

The formation and evolution of the microstructure for cement paste during hydration are readily obtained by this hydration model, which is rather difficult for laboratory measurement. Generally, the HYMOSTRUC3D model is feasible to directly exhibit the evolution of the microstructure characteristics (e.g., tortuosity, pore size and connectivity) of cement-based systems. Meanwhile, it has been widely applicable to predict the permeability (Zhang et al. 2013; Zhang 2017), elastic modulus (Mazaripour et al. 2018), ionic diffusivity (Zhang et al. 2012) and fracture propagation (Qian et al. 2017) of cementitious materials.

3. Modeling permeability of cement paste

3.1 Simulation of the pore-scale flow

Moisture transport at the microscale level almost occurs exclusively in capillary pores of cement paste. The fluid flow in these pores (i.e., pore-scale flow) is usually described by Navier-Stokes equations (Ye et al. 2006; Picandet et al. 2011). By combining the motion equation (Navier-Stokes hydrodynamic equation) with mass conservation (continuity equation), the steady-state incompressible fluid flow in cement paste may be described by Eqs. (4) and (5) (Yang et al. 2012; Zalzale and McDonald 2012; Sun et al. 2014; Li et al. 2017a),

\[ \nabla u = 0 \]  
\[ F + \nabla \mu \left( \nabla u + (\nabla u)^T \right) - \rho u \nabla u - \nabla p = 0 \]  

where \( \rho \) is fluid density (kg/m\(^3\)); \( u \) is fluid velocity (m/s), \( p \) is hydraulic pressure (Pa) and \( \mu \) is dynamic viscosity of the fluid (Pa·s). \( \nabla \) and \( \nabla^2 \) are spatial operators (/m and /m\(^2\)).

Equations (4) and (5) are subject to the appropriate initial condition below,

\[ p|_{t=0} = p_0, \quad u|_{t=0} = u_0 \quad \text{(Initial boundary)} \]  

and the boundary conditions below.

\[ p|_{\text{inlet}} = p_{in} \quad \text{(Inlet boundary)} \]  
\[ p|_{\text{outlet}} = p_{out} \quad \text{(Outlet boundary)} \]  
\[ u = 0 \quad \text{(No slip boundary)} \]  

The above equations could be solved by FEM, where the geometry entity of continuous media is discretized into discrete elements connecting with each other by nodes. The solution of the differential equations is transformed into a set of linear equations by piecewise interpolation of the shape function in the elements. Equations (4) to (9) could be discretized by the variation principle, given by,

\[ [K]\{\psi\} = \{F\} \]  

where \([K]=\sum_i^K\rangle\) is conductivity matrix of flow.

![Fig. 3 Hydration process in the central profile of the samples with w/c = 0.4.](image-url)
\[
\psi = \sum \psi
\]

is the pressure and the pore-scale permeability test of cement paste, by which it could be assumed that the composite material (i.e., cement paste) is homogeneous in a statistical sense (Li 2005). Based on Darcy’s law, the intrinsic permeability of RVE (i.e., cement paste) is usually measured in the laboratory by permeability tests and is written as.

\[
\kappa = \frac{LQ \mu}{S \Delta P}
\]

where \( L \) is the length of flow path (m), \( \Delta P \) is the hydraulic pressure difference (m), \( S \) is the cross-sectional area perpendicular to flow direction (m²), and \( Q \) represents the flow rate (m³/s).

The permeability of cement paste varies with the evolution of the micropore structure (e.g., pore size and pore continuity) during hydration process. For the freshly mixed cement paste, it is of the order of \( 10^{-13} \) to \( 10^{-15} \) m²; with the progress of hydration, the capillary porosity decreases, so does the magnitude of permeability. In respect to the permeability of hardened cement paste, reported data can span several orders of magnitude typically from \( 10^{-15} \) to \( 10^{-22} \) m². Compared with many other porous materials, the intrinsic permeability of cement paste is surprisingly low. As a result, its measurement is particularly difficult since the flux of water through the tested sample is extremely slow at moderate pressures. Hence, the parameter of permeability is less often measured in cement paste and there is still a paucity of experimental data.

In this study, valuable data collated from twenty publications are summarized in Table 1 to illustrate the

| Literature | Test method | w/c | Hydration age (d) | Intrinsic permeability (m²) |
|------------|-------------|-----|------------------|-----------------------------|
| Nyame and Illston (1981) | Pressure-induced (water) | 0.35 | 1–28 | 2.5×10^{-17}–6.4×10^{-20} |
| Banthia and Mindess (1989) | Pressure-induced (water) | 0.35 | 1–28 | 2.5×10^{-17}–6.4×10^{-20} |
| Vichit-Vadakan and Scherer (2002) | Beam bending (water) | 0.4 | 3–14 | 4×10^{-21}–3×10^{-22} |
| Ye (2005) | Pressure-induced (water) | 0.6 | 5–14 | 10^{-15}–6×10^{-21} |
| Grasley et al. (2006) | Hollow dynamic pressurization (water) | 0.30 | 28 | 10^{-19}–2×10^{-20} |
| Wei et al. (2017) | Radial flow-through (water) | 0.325 | 28 | 10^{-18}–10^{-22} |

Table 1 Experimental data of the intrinsic permeability of cement paste.
evolution of permeability during hydration. It is found that there is substantial variability in the measured permeability, depending on the sample properties (e.g., chemical composition, w/c and degree of hydration), sample preparation (e.g., drying and curing protocols), permeation fluid (e.g., water and oxygen) and test method. Since the repeatability of experimental measurements is not guaranteed, it might be an alternative to predict the permeability of cement paste by numerical modeling methods with low cost and high operability.

A numerical test method is proposed in this study to predict the permeability of hydrating cement paste. With the microstructure of cement paste practically characterized by HYMOSTRUC3D model, the pore-scale flow through the numerical sample could be simulated by solving the aforementioned equations. To determine the permeability of the sample, a detailed description of the numerical test is presented hereinafter.

For a numerical test, the hydration products and unhydrated cement particles in the RVE sample are assumed impermeable because their permeability is extremely negligibly low. Thus, the pore-scale flow in micropores is solely taken into account in this study. An example considering a steady water flow process is outlined in Fig. 4. The pressures of \( p_{\text{in}} \) and \( p_{\text{out}} \) are applied to the inlet and outlet boundaries (i.e., the bottom and top surfaces of the sample, respectively). Since the fluid flow in pore network is the main issue to be studied and the other side surfaces of the cube are usually sealed, no-slip conditions are employed on the outer surfaces of hydration product (pore walls) and other surfaces of the sample. With the pore-scale flow velocity field calculated by FEM, the intrinsic permeability of this sample could be determined by two approaches as below,

\[
\kappa = \frac{\bar{\mu} \mu}{\bar{J} \gamma} = \frac{1}{V \bar{J} \gamma} \int \mu \frac{dV}{V} = \frac{1}{V \bar{J} \gamma} \int \frac{dV}{V} \mu
\]  

(12)

where \( J \) is the hydraulic gradient, \( V \) denotes the volume of the pores in the tested sample (m³), \( \bar{\mu} \) and \( \bar{J} \) are the average flow velocity and hydraulic gradient in the pores, and \( \gamma \) is denoted as the specific unit weight of fluid (i.e., water).

Equation (12) reflects the effective transport response by volumetrically averaging the internal flow field over the entire domain of the heterogeneous microstructure, while Eq. (13) represents the average permeability through integrating the velocity distribution on the inlet (or outlet) surface. Although Eq. (12) might be more reasonable to describe the homogenized properties of a heterogeneous microstructure, yet Eq. (13) is used hereinafter to calculate the permeability of numerical sample since it is consistent with the measurement in the laboratory test. The aforementioned formulations are numerically implemented in the commercial FE software, COMSOL Multiphysics, version 5.3 (marketed by COMSOL Incorporated, Burlington, Massachusetts, USA), which is a powerful tool providing full access to solve partial differential equations. It is noted that the main concern of this present study is to represent the overall material properties of hydrating cement paste (i.e., water permeability). The local characteristics in the microstructure associating with tortuosity and pore throat size are not the important point. Therefore, this present work is focused on the total porosity of numerical samples and the average permeability obtained from Eq. (13) with respect to hydration process, which will be primarily tested and evaluated hereinafter.

4. Validation of the numerical test

4.1 3D Poiseuille flow in a square channel

In order to validate the numerical test described in Section 3, a series of benchmark tests are undertaken to simulate the 3D Poiseuille flow in a square channel sized by \( L \times b \times b \) (\( L \gg b \)). The samples with channel width determined as 0 to 100 \( \mu \)m and length kept constant as 500 \( \mu \)m are generated and then \( p_{\text{in}} = 1.0 \) Pa and \( p_{\text{out}} = 0.0 \) Pa are applied to the inlet and outlet surfaces of the model, respectively. Through the numerical simulation, the velocity distribution profile of water flowing through cubic channels with different widths is derived as shown in Fig. 5 and the intrinsic permeability is also predicted as presented in Fig. 6. Additionally, in respect to the cubic channel, the 3D Poiseuille flow can be computed in closed form using the theoretical solutions, in which the flow velocity and theoretical permeability are given as below (Hecht and Harting 2010; Zhang et al. 2013),

\[
u_s(x,y) = \frac{Vp}{2\pi} \left[ b^3 y - y^3 - \frac{8b^3}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n \cos(2n+1)\pi x/b \cos(2n+1)\pi y/b}{(2n+1)\cos(2n+1)\pi/2} \right]
\]  

(14)
\[
\kappa = \frac{b^2}{4} \left[ \frac{1}{3} - \frac{64}{\pi} \sum_{n=0}^{\infty} \frac{\tanh \left( \frac{\pi}{2} (2n+1) \right)}{(2n+1)^2} \right] \approx 0.03514b^2 \tag{15}
\]

where \( x \in [-b/2, b/2] \) and \( y \in [-b/2, b/2] \); and \( u_z(x,y) \) is the velocity in the \( z \) direction at the location of \((x,y,z)\).

The comparison between numerical and theoretical results is plotted in Figs. 5 and 6. Figure 5 presents that the maximum inflow velocity is located in the center across the pore channel and diminishes uniformly to zero at the walls where the nonslip boundary conditions for viscous fluid are applied. Along the length direction of the pore channel, the velocity profile is uniform and symmetric. For a larger width of the square channel, a higher flow velocity is observed on account of the increased cross-sectional area perpendicular to flow direction.

Figure 6 reveals that a parabolic relationship is obeyed between the intrinsic permeability and channel width. Generally, it is evident from Figs. 5 and 6 that the numerical results agree perfectly well with the theoretical data, which therefore supports the possibility of applying the proposed method to water transport analysis in cementitious materials.

### 4.2 Flow through cube containing periodic array of mono-sized spheres

The proposed numerical test method is further validated in comparison with the theoretical solution for flow through cube containing a periodic array of mono-sized spheres, i.e., simple-cubic (SC), body-centered-cubic (BCC) and face-centered-cubic (FCC). Cubic samples with a side of 100 \( \mu \text{m} \) are generated where the mono-sized spherical solids are imbedded at the specific location for SC, BCC and FCC cases. Water flow through the microstructure of the sample is simulated under the water pressures of \( p_{\text{in}} = 1.0 \text{ Pa} \) and \( p_{\text{out}} = 0.0 \text{ Pa} \), and then the intrinsic permeability of numerical samples with different porosities is estimated. For comparison, the theoretical permeability of cube containing periodic array of mono-sized spheres is given by Larson and Higdon (1989) as,

\[
\kappa = V_0 / (6\pi a C_j) \tag{16}
\]

where \( V_0 \) is the volume of the unit cube with length of \( L \) (m\(^3\)); for SC, BCC and FCC, \( V_0 \) is \( L^3 \), \( 1/2L^3 \), and \( 1/4L^3 \), respectively. \( a \) is the radius of solid sphere (m), and \( C_j \) is the drag coefficient, expressed by Sangani and Acrivos (1982) as,

\[
C_j = \sum_{n=0}^{\infty} \alpha_\phi \chi^n, \quad \chi = \left( \frac{\phi}{\phi_{\phi_{\max}}} \right)^{1/3} \tag{17}
\]

where \( \alpha_\phi \) could be found in the literature (Sangani and Acrivos 1982). \( \phi \) is the volume fraction of spheres and \( \phi_{\phi_{\max}} \) is the maximum when the solid spheres are in the touching configuration. For SC, BCC and FCC, \( \phi \) is \( 4\pi a^3 / 3L^3 \), \( 8\pi a^3 / 3L^3 \), and \( 16\pi a^3 / 3L^3 \), respectively, and \( \phi_{\phi_{\max}} \) is \( \pi / 6, \sqrt{3}\pi / 8 \) and \( 2\pi / 6 \), respectively.

Flow velocity field in the pores for cubic unit cells with the porosity of 0.6 is depicted in Fig. 7. It is ap-
parent that the arrays of the sphere particles have a pronounced influence on the flow behavior and tortuous flow of fluid develops at the clusters of these particles. This may contribute to the uneven distribution of velocity and the diversity of permeability associated with structural characteristics.

Figure 8 displays the comparison of simulated and theoretical intrinsic permeability as a function of porosity. It appears that the intrinsic permeability for the microstructure augments remarkably with the increase of its porosity. Moreover, the permeability for SC is largest attributable to the pore characteristics (e.g., tortuosity and pore throat size), which follows a similar regulation of velocity distribution as plotted in Fig. 7. In the microstructure of hydrating cement paste, the tortuosity and pore throat size could be explicitly modeled while not quantitatively evaluated in this study. The tortuosity effect could further lengthen the flow path, which may decrease the permeability of cement paste (Li et al. 2016c) and a small pore throat size may weaken the flow capacity of the pore network for water transport. In general, the simulated results are in good agreement with the data obtained from theoretical calculations. The proposed numerical test is able to simulate the pore-scale flow in the microstructure and predict the permeability of cement-based material.

5. Prediction of the permeability of cement paste

In order to predict the permeability directly from the morphology of the 3D microstructure, numerical simulations are performed using the proposed numerical test method. It is widely accepted that the minimum particle size distribution in CEM I 42.5 N is normally 0.2 to 0.5 µm. As a multi-phase composite, the microstructure of hydrating cement paste is extremely complicated, a huge amount of calculation is demanded when introducing smaller particle size distribution of cement in the numerical modeling. In consideration of the computational capacity, the size range of cement particles is taken as 5 to 50 µm following the Rosin-Rammler curve [cf. Eq. (1)] with the diameter of particles lower than 5 µm ignored for simplification. Numerical samples sized by 100 µm×100 µm×100 µm are generated with different w/c and curing ages. In general, the simulated results are in good agreement with the data obtained from theoretical calculations. The proposed numerical test is able to simulate the pore-scale flow in the microstructure and predict the permeability of cement-based material.

![Fig. 8 Simulated and theoretical intrinsic permeability as a function of porosity.](image)

![Fig. 7 Flow velocity field in the cubic unit cells with the porosity of 0.6 (Unit: m/s).](image)

In the microstructure of hydrating cement paste, the tortuosity and pore throat size could be explicitly modeled while not quantitatively evaluated in this study. The tortuosity effect could further lengthen the flow path, which may decrease the permeability of cement paste (Li et al. 2016c) and a small pore throat size may weaken the flow capacity of the pore network for water transport. In general, the simulated results are in good agreement with the data obtained from theoretical calculations. The proposed numerical test is able to simulate the pore-scale flow in the microstructure and predict the permeability of cement-based material.
pressure and flow velocity in the simulated sample with w/c = 0.45 at different curing ages (1 d, 3 d, 7 d and 30 d). Water flow is restricted by the impermeable phase composed of anhydrous cement and hydration product, and only passes through the liquid-filled pores. It is notable that the pore water pressure and flow velocity are both nonuniformly distributed, which are apparently affected by the heterogenous microstructure. The hydraulic discontinuities of different phases, induced by the complicated microstructural heterogeneity of cement paste are apparently observed. The hydraulic pressure diminishes progressively in the direction of water movement from the maximum at the bottom surface to the minimum on the up boundary. Distribution of flow velocity suggests that water flow in heterogeneous cement composite does not follow a straight streamline, whereas the randomly distributed products cause tortuosity effect that forces the water to flow around them. The penetration of water is constrained into a tortuous configuration and follows the liquid-filled pore network. With the progress of cement hydration reactions, more impermeable phases (hydration products) generate and connect together gradually. As a result, the overall impermeable phases (hydration products) generate and connect together gradually. As a result, the overall impermeability of cement paste shows a dramatic improvement since the hydration products fill up the empty or water-filled pore spaces present in the cement paste. Generally, the permeability of cement paste is greatly affected versus the curing age under the combined effects of dilution and tortuosity, which are similar to the simulated results of concrete referred to authors’ previous work (Li et al. 2016b, 2016c, 2017b).

Another interesting phenomenon to notice from Fig. 10 is revealed that the influence of the porous skeleton on the water flow is pronounced. It is obviously shown that with the curing age increasing, the pore size decreases, especially the pore throat size, which could lower down the pore connectivity as shown in Fig. 10. When water impinges into the porous structure of cement paste, the fluid velocity accelerates dramatically in the small-size pore throat, where a larger fluid velocity (red arrows) can be observed. The size and distribution of pore throat in the microstructure correlate tightly to the water transport behavior, which might be a dominant factor in the permeability of cement paste. Due to the fact that the 2D model would underestimate the transport property for hardly interpreting the influence of pore throat in spatial flow, the 3D model is definitely necessary to better estimate the evolution of the microstructure and permeability of cement paste.

For the sake of reflecting the complicated flow regime in the microstructure of cement paste, the Reynolds number is determined based on the fluid velocity field, given by,

$$\text{Re} = \frac{ud}{v}$$

where $d$ is the diameter of the pore channel (m). For instance, in Fig. 10(a) $u < u_{\text{max}} = 4.0 \times 10^{-6}$ m/s, and $d < L = 100$ $\mu$m, and thus $\text{Re} < 3.97 \times 10^{-4} << 1$. The Reynolds number suggests that water flow situation related to cementitious material may belong to the laminar flow regime and follow Darcy’s law which identifies similar patterns with the experimental measurement.

The permeability of the cement paste samples with different w/c versus porosities is then computed, and compared with other numerical results (Zalzale and McDonald 2012; Yu et al. 2018a) and experimental data (Hu and Stroeven 2011; Wong et al. 2012), as shown in Fig. 11. It is shown that the simulated permeability of cement paste increases with the porosity, which shows a consistent trend towards that can be observed from the published numerical and experimental results (Hu and Stroeven 2011; Wong et al. 2012; Zalzale and McDonald 2012; Yu et al. 2018a).

It is mentioned that the simulated permeability approximates in the same magnitude of that from other numerical simulations (Zalzale and McDonald 2012; Yu et al. 2018a) and locates in the intermediate range of them. This difference is probably partially due to that different assumptions inherent in these numerical algorithms may affect the permeability results. Meanwhile, cement particles with size range of 5 to 50 $\mu$m are involving in numerical study, while in reality the diameter of cement particle is usually scaling from 0.1 to 50 $\mu$m. When more smaller particles incorporate, the hydration process is more sufficient to react, resulting in generating more hydration products, which will decrease the volume of pore space and the permeability of cement paste. As Ye et al. (2006) found that the minimum size of cement particles scales from 2 $\mu$m to 1 $\mu$m, the permeability of hardened cement paste at 30 d reduces approximately 2 to 3 orders of magnitude.

In Fig. 11, the simulated permeability presents several orders of magnitude larger than experimental data reported in the literature (Hu and Stroeven 2011; Wong et al. 2012). The differences may probably attribute to that the saturation conditions of specimens in simulations and experiments are generally not the same. Actually, Darcy’s
law utilized in the conventional laboratory measurement for water permeability requires the specimens to be fully saturated. This is readily postulated in numerical simulation, whereas the full saturation state is difficult to realize in practice, leading to the measured permeability pertaining to partially saturated materials rather than

Fig. 10 Hydraulic pressure (Unit: Pa; Left figure) and flow velocity (Unit: m/s; Right figure) of the simulated samples with w/c = 0.45 at different curing ages.
saturated one (Li et al. 2016a).

In spite of some simplifications and assumptions made, the reasonably good agreement of the predicted permeability and that from other numerical and experimental results indicates that the proposed method can be practically used for modeling transport process in hydrating cement paste. However, the proposed numerical test method may still lack the desired accuracy in predicting the permeability of a highly complex and heterogeneous microstructure. To improve the method’s predictive capability and obtain quantitative evaluation results, more detailed investigations into geometrical microstructure and transport mechanism might be demanded for considering the smaller cement particles and different saturated state in future.

Figure 12 shows the evolution of intrinsic permeability against curing age and degree of hydration. A non-linear relationship of permeability with respect to curing age and degree of hydration is exhibited, and is attributable to the complicated chemical and physical hydration mechanisms. As the hydration rate gradually slows down, the permeability decreases in the similar pattern and displays a tendency to be stable for a long curing age, which is consistent with the results published in the literature (Yu et al. 2018a). The hydration process of cement paste is almost completed after a long time, and its permeability would be basically kept stable. However, the permeability of cementitious material might decrease a little when the cement-based material comes into contact with the water again because of the autogenous self-healing capacity, especially for cracked cementitious materials (Huang et al. 2016; Suleiman and Nehdi 2018).

Generally, the numerical method is effective and reasonable to predict the permeability of hydrating cement paste. The evolution process of microstructure and permeability could be practically simulated and the results might be expected to provide basic material parameters for mesoscale modeling and beneficial to the multiscale modeling and coupled multiphysics analysis for concrete engineering.

6. Conclusions
In this paper, a numerical test method based on 3D FEM is developed to predict the permeability of cement paste. Based on the HYMOSTRUC3D model, the multi-phase microstructure of hydrating cement paste is established for numerical sampling. Subsequently, the entity of the model containing capillary pores only is meshed to achieve regular grids by solid tetrahedron elements using DTM. According to pore-scale flow theory, water transport through the microstructure induced by pressure-gradient is simulated and the corresponding water permeability is predicted using 3D FEM. Several simulations are conducted to verify the developed method in comparison with the analytical solution, numerical results and experimental data obtained from the literature. Finally, the evolution of permeability for cement paste with various w/c and curing ages is estimated, and the influence of the micropore structure on water flow characteristics is investigated. From the study, the following conclusions can be drawn:

(1) The simulated results obtained from the proposed numerical test method are reasonably consistent with the theoretical solution, numerical results and experimental data obtained from the literature. It might...
be an efficient approach to simulate the pore-scale flow in the microstructure and predict the corresponding permeability of porous media.

(2) Water flow characteristics (e.g., hydraulic pressure distribution and flow velocity vectors) through the microstructure of cement paste are well captured by the pore-scale flow modeling. The effects of pore network connection and pore throat in 3D space influence the fluid flow behavior in a notably significant manner. The results indicate that 3D modeling is necessary to establish the relations between microstructure and transport properties of the cementitious media.

(3) The predicted permeability of cement paste decreases as the hydration proceeds and with the diminution of w/c for a lower porosity, showing a similar tendency with other numerical models and experimental data from the literature. During the hydration process, the permeability is strongly dependent on the micropore structure: the dilution effect caused by impermeable phase (i.e., anhydrous cement and hydration product) and the tortuosity effect resulting from the highly heterogeneous pore network, both of which can lead to the decrease of permeability.

The effectiveness and reliability of such a simulation for pore-scale flow depends largely on the description of the micropore structure. In this paper, the microstructure of hydrating cement paste is characterized by computer-generated model and the size of cement particles is restrained in the range of 5 to 50 μm. However, these simplifications and assumptions may have impacts on the accuracy level of the permeability prediction. In future, more advanced experimental measurements for the pore structure characterization of cement paste (e.g., X-ray computed microtomography) should be realized as model input to simulate the pore-scale flow with high accuracy.

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References
Banala, A. and Kumar, A., (2017). “Numerical simulations of permeability of plain and blended cement pastes.” International Journal of Advances in Engineering Sciences and Applied Mathematics, 9(2), 67-86.
Banthia, N. and Mindess, S., (1989). “Water permeability of cement paste.” Cement and Concrete Research, 19(5), 727-736.
Bentz, D. P., (1997). “Three-dimensional computer simulation of portland cement hydration and microstructure development.” Journal of the American Ceramic Society, 80(1), 3-21.
Bishnoi, S. and Scrivener, K. L., (2009). “μC: a new platform for modelling the hydration of cements.” Cement and Concrete Research, 39(4), 266-274.
Bittnar, Z., (2006). “Microstructure-based micromechanical prediction of elastic properties in hydrating cement paste.” Cement and Concrete Research, 36(9), 1708-1718.
Chen, S. H., (2019). “Computational geomembranes and hydraulic structures.” Singapore: Springer Singapore.
Cui, L. and Cahyadi, J. H., (2001). “Permeability and pore structure of OPC paste.” Cement and Concrete Research, 31(2), 277-282.
Di Bella, C., Wyzykowski, M., Griffa, M., Termkhajornkit, P., Chanvillard, G., Stang, H., Eberhardt, A. and Lura, P., (2015). “Application of microstructurally-designed mortars for studying early-age properties: microstructure and mechanical properties.” Cement and Concrete Research, 78, 234-244.
Dolado, J. S. and Van Breugel, K., (2011). “Recent advances in modeling for cementitious materials.” Cement and Concrete Research, 41(7), 711-726.
Gao, Y., Feng, P. and Jiang, J. Y., (2018). “Analytical and numerical modeling of elastic moduli for cement based composites with solid mass fractal model.” Construction and Building Materials, 172, 330-339.
Grasley, Z. C., Scherer, G. W., Lange, D. A. and Valenza, J. J., (2007). “Dynamic pressurization method for measuring permeability and modulus, part II: cementitious materials.” Materials and Structures, 40(7), 711-721.
Hall, C. and Hoff, W. D., (2012). “Water transport in brick, stone and concrete.” 2nd ed. London: Spon Press.
Hecht, M. and Harting, J., (2010). “Implementation of on-site velocity boundary conditions for D3Q19 lattice Boltzmann simulations.” Journal of Statistical Mechanics: Theory and Experiment, 2010(01), P01018.
Hlobil, M., Šmilauer, V. and Chanvillard, G., (2016). “Micromechanical multiscale fracture model for compressive strength of blended cement pastes.” Cement and Concrete Research, 83, 188-202.
Hu, J. and Stroeven, P., (2011). “Application of image analysis to assessing critical pore size for permeability prediction of cement paste.” Image Analysis & Stereology, 22(2), 97-103.
Huang, H., Ye, G. and Pel, L., (2016). “New insights into autogenous self-healing in cement paste based on nuclear magnetic resonance (NMR) tests.” Materials and Structures, 49(7), 2509-2524.
Koster, M., Hannawald, J. and Brameshuber, W., (2006). “Simulation of water permeability and water vapor diffusion through hardened cement paste.” Computational Mechanics, 37(2), 163-172.
Larbi, B., Dridi, W., Dangla, P. and Le Bescop, P., (2016). “Link between microstructure and tritiated water diffusivity in mortars: impact of aggregates.” Cement and Concrete Research, 82(1), 92-99.
Larson, R. E. and Higdon, J. J., (1989). “A periodic grain...
consolidation model of porous media.” Physics of Fluids A: Fluid Dynamics, 1(1), 38-46.
Li, K., Stroeven, M., Stroeven, P. and Sluys, L. J., (2016a). “Investigation of liquid water and gas permeability of partially saturated cement paste by DEM approach.” Cement and Concrete Research, 83, 104-113.
Li, K., Stroeven, M., Stroeven, P. and Sluys, L. J., (2017a). “Effects of technological parameters on permeability estimation of partially saturated cement paste by a DEM approach.” Cement and Concrete Composites, 84, 222-231.
Li, X. X., Chen, S. H., Xu, Q. and Xu, Y., (2017b). “Modeling the three-dimensional unsaturated water transport in concrete at the mesoscale.” Computers & Structures, 190, 61-74.
Li, X. X., Xu, Q. and Chen, S. H., (2016b). “An experimental and numerical study on water permeability of concrete.” Construction and Building Materials, 105, 503-510.
Li, X. X., Xu, Y. and Chen, S. H., (2016c). “Computational homogenization of effective permeability in three-phase mesoscale concrete.” Construction and Building Materials, 121, 100-111.
Liu, R., Xiao, H. G., Li, H., Sun, L., Pi, Z. Y., Waqar, G. Q., Du T. and Yu, L., (2018). “Effects of nano-SiO2 on the permeability-related properties of cement-based composites with different water/cement ratios.” Journal of Materials Science, 53(7), 4974-4986.
Mazaheripour, H., Faria, R., Ye, G., Schlangen, E., Granja, J. and Azenha, M., (2018). “Microstructure-based prediction of the elastic behaviour of hydrating cement pastes.” Applied Sciences, 8(3), 442.
Mehta, P. K. and Monteiro, P. J., (2013). “Concrete: microstructure, properties, and materials.” 4th ed. New York: McGraw-Hill.
Nyame, B. K. and Illston, J. M., (1981). “Relationships between permeability and pore structure of hardened cement paste.” Magazine of Concrete Research, 33(116), 139-146.
Ouzia, A. and Scrivener, K., (2019). “The needle model: a new model for the main hydration peak of alite.” Cement and Concrete Research, 115, 339-360.
Phung, Q. T., Maes, N., De Schutter, G., Jacques, D. and Ye, G., (2013). “Determination of water permeability of cementitious materials using a controlled constant flow method.” Construction and Building Materials, 47, 1488-1496.
Phung, Q. T., Maes, N., Jacques, D., De Schutter, G. and Ye, G., (2016). “Investigation of the changes in microstructure and transport properties of leached cement pastes accounting for mix composition.” Cement and Concrete Research, 79, 217-234.
Picandet, V., Rangeard, D., Perrot, A. and Lecompte, T., (2011). “Permeability measurement of fresh cement paste.” Cement and Concrete Research, 41(3), 330-338.
Qian, Z. W., Schlangen, E., Ye, G. and van Breugel, K., (2017). “Modeling framework for fracture in multiscale cement-based material structures.” Materials, 10(6), 587.
Reinhardt, H. W., (1997). “Penetration and permeability of concrete: barriers to organic and contaminating liquids (RILEM report 16).” London: Taylor & Francis Group.
Rose, J. L. and Grasley, Z. C., (2017). “Comparison of permeability of cementitious materials obtained via poromechanical and conventional experiments.” Journal of Materials in Civil Engineering, 29(9), 04017083.
Sangani, A. S. and Acrivos, A., (1982). “Slow flow through a periodic array of spheres.” International Journal of Multiphase Flow, 8(4), 343-360.
Suleiman, A. R. and Nehdi, M. L., (2018). “Effect of environmental exposure on autogenous self-healing of cracked cement-based materials.” Cement and Concrete Research, 111, 197-208.
Sun, X., Dai, Q. and Ng, K., (2014). “Computational investigation of pore permeability and connectivity from transmission X-ray microscope images of a cement paste specimen.” Construction and Building Materials, 68, 240-251.
Tang, S. W., Li, Z. J., Zhu, H. G., Shao, H. Y. and Chen, E., (2014). “Permeability interpretation for young cement paste based on impedance measurement.” Construction and Building Materials, 59, 120-128.
Tchamba, J. C. and Bikoko, T. G. L. J., (2016). “Study of transfer properties on fresh cement pastes; laboratory experiments: discontinuous measurements using a permeameter.” Journal of Materials Science Research, 5(2), 23-32.
Thomas, J. J., Biernacki, J. J., Bullard, J. W., Bishnoi, S., Dolado, J. S., Scherer, G. W. and Luttgte, A., (2011). “Modeling and simulation of cement hydration kinetics and microstructure development.” Cement and Concrete Research, 41(12), 1257-1278.
Tian, Z. H. and Bian, C., (2013). “Numerical modeling of elastic modulus for cement paste using homogenization method.” Journal of Wuhan University of Technology - Mater. Sci. Ed., 28(4), 751-760.
van Breugel, K., (1995). “Numerical simulation of hydration and microstructural development in hardening cement-based materials (I) theory.” Cement and Concrete Research, 25(2), 319-331.
Vichit-Vadakan, W. and Scherer, G. W., (2002). “Measuring permeability of rigid materials by a beam-bending method, part III: cement paste.” Journal of the American Ceramic Society, 85(6), 1537-1544.
Wang, L. C. and Bao, J. W., (2017). “Investigation on chloride penetration into unsaturated concrete under short-term sustained tensile loading.” Materials and Structures, 50(5), 227.
Wong, H. S., Zimmerman, R. W. and Buenfeld, N. R., (2012). “Estimating the permeability of cement pastes
and mortars using image analysis and effective medium theory.” *Cement and Concrete Research*, 42(2), 476-483.

Wong, H. S., Zobel, M., Buenfeld, N. R. and Zimmerman, R. W., (2009). “Influence of the interfacial transition zone and microcracking on the diffusivity, permeability and sorptivity of cement-based materials after drying.” *Magazine of Concrete Research*, 61(8), 571-589.

Xu, Y., Xu, Q., Chen, S. H. and Li, X. X., (2017). “Self-restraint thermal stress in early-age concrete samples and its evaluation.” *Construction and Building Materials*, 134, 104-115.

Yang, B. H., Wu, A. X., Wang, C. L., Niu, W. X. and Liu, J. Z., (2012). “Three-dimensional simulation of pore scale fluid flow in granular ore media with realistic geometry.” *Transactions of Nonferrous Metals Society of China*, 22(12), 3081-3086.

Ye, G., (2005). “Percolation of capillary pores in hardening cement pastes.” *Cement and Concrete Research*, 35(1), 167-176.

Ye, G., Lura, P. and van Breugel, K., (2006). “Modelling of water permeability in cementitious materials.” *Materials and Structures*, 39(9), 877-885.

Yu, P., Duan, Y. H., Chen, E., Tang, S. W. and Wang, X. R., (2018a). “Microstructure-based fractal models for heat and mass transport properties of cement paste.” *International Journal of Heat and Mass Transfer*, 126, 432-447.

Yu, Z. Q., Ni, C. X., Tang, M. L. and Shen, X. D., (2018b). “Relationship between water permeability and pore structure of portland cement paste blended with fly ash.” *Construction and Building Materials*, 175, 458-466.

Zalzale, M. and McDonald, P. J., (2012). “Lattice Boltzmann simulations of the permeability and capillary adsorption of cement model microstructures.” *Cement and Concrete Research*, 42(12), 1601-1610.

Zhang, J. Z., Bian, F., Zhang, Y. R., Fang, Z. F., Fu, C. Q. and Guo, J., (2018). “Effect of pore structures on gas permeability and chloride diffusivity of concrete.” *Construction and Building Materials*, 163, 402-413.

Zhang, M. Z., (2017). “Pore-scale modelling of relative permeability of cementitious materials using X-ray computed microtomography images.” *Cement and Concrete Research*, 95, 18-29.

Zhang, M. Z., Ye, G. and van Breugel, K., (2012). “Modeling of ionic diffusivity in non-saturated cement-based materials using lattice Boltzmann method.” *Cement and Concrete Research*, 42(11), 1524-1533.

Zhang, M. Z., Ye, G. and van Breugel, K., (2013). “Microstructure-based modeling of permeability of cementitious materials using multiple-relaxation-time lattice Boltzmann method.” *Computational Materials Science*, 68, 142-151.

Zheng, J. J., Zhou, X. Z. and Wu, Z. M., (2010). “A simple method for predicting the chloride diffusivity of cement paste.” *Materials and Structures*, 43(1-2), 99-106.

Zhou, W., Duan, L., Tang, S. W., Chen, E. and Hanif, A., (2019). “Modeling the evolved microstructure of cement pastes governed by diffusion through barrier shells of C-S-H.” *Journal of Materials Science*, 54(6), 4680-4700.

Zienkiewicz, O. C. and Taylor, R. L., (2005). *The finite element method for solid and structural mechanics.* 6th ed. Oxford, England: Butterworth-Heinemann.