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Microstructure-based fractal models for heat and mass transport properties of cement paste

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ABSTRACT

In this study, a computer simulation for the microstructure, heat and mass transport properties of cement paste is established. Constituent phases and pore structure of cement paste are analyzed in detail and a three-level representation of multiscale microstructure of cement paste is constructed based on some reasonable assumptions. Simulated results are comprehensively analyzed and verified, which proves the reliability and efficiency of the presented simulation. Based on the simulated microstructure, transport properties of cement paste are investigated with the aid of fractal theory. Fractal features of cement paste are obtained through the simulated microstructure. Then, fractal models are applied to predict transport properties (permeability, diffusivity and thermal conductivity) of cement paste. In order to verify the fractal models, experimental data and results from other models in literature are adopted to make comparisons, which shows a reasonable consistency and proves the reliability and efficiency of the presented fractal models.

1. Introduction

Transport properties of cement paste are of great concern due to their great influence on the safety and durability of cement-based structures [1]. On one hand, thermal and hygric properties of cement paste are deemed to be crucial to the cracking phenomena at early ages [2]. On the other hand, structural performance of cement-based structures during their service time is closely related to the deterioration of material properties, which is greatly attributed by the heat and mass transfer inside the microstructure [2]. Therefore, it is essential to investigate microstructure characteristics of cement paste and develop appropriate simulation and model to reveal the relationship between microstructure characteristics and macroscopic properties.

In general, cement paste is considered as a typical multi-scale porous medium with a large number of pores whose size is perhaps from nano to micro scale. Various experimental techniques have been developed till now for the assessment of pore structure of cement paste [3]. Obviously, each of the existing techniques only corresponds to pores with a certain scale. For instance, nitrogen adsorption test is widely used to characterize small nano pores with size from several to tens of nanometers [4]. While some capillary pores with size possibly from hundreds of nanometers to tens of micrometers need to be detected by back-scattered electron microscopy (BSE) image test [5]. Comparatively speaking, mercury intrusion porosimetry (MIP) test is able to measure a wide scale of pores whose size lies between 3 nm and 100 μm [6]. Despite several limitations of MIP test, it is still considered as an "effective" method for analyzing pore structure characteristics [6]. It is worth pointing out that specimens need to be dried in advance for nitrogen adsorption, electron microscopy and MIP tests. In addition, some specimens may be damaged to some extent and cracks may generate when certain pressure is applied onto specimens during nitrogen adsorption and MIP tests. As laboratory tests are sometimes time-consuming and expensive, several computer simulations (Durability Models of Concrete Model "DuCOM" by Maekawa et al. [7,8], "HYMOSTRUC" by Breugel [9–11], "μic" by Bishnoi and Scrivener [12,13], "CEMHYD3D" by Bentz and Garboczi [14,15]) have been developed to investigate the microstructure of cement paste during the hydration [7–15]. However, each of these simulations focuses on a specific perspective and cannot reflect the overall pore structure characteristics.

Many kinds of experimental tests have been developed to investigate transport properties of cement-based materials, which mainly include permeability, diffusivity and thermal conductivity. As an important hydraulic parameter for characterizing mass transport properties, permeability is one of the most important

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indicators for the durability of cement-based materials. The diffusion of dissolved harmful chemical species in cement-based materials has a strong correlation with their pore structure, affecting the durability of cement-based materials. Additionally, cement-based materials are sensitive to heterogeneous temperature gradients, which may lead to cracking on a microscopic or macroscopic scale [16]. Therefore, understanding thermal properties of cement-based materials is essential. Although many kinds of experimental techniques have been developed to measure transport properties of cement paste, most of them usually have complex test procedures, and experimental results often exhibit high variability due to the disordered and complicated pore structure [17]. In conclusion, there is no widespread recognition for the test methods of transport properties [4]. In the past decade, with the development of computer technology, many kinds of computer models have been proposed to investigate transport properties of cement paste. In most of the existing models, transport properties are obtained based on relatively mature algorithms [18,19], e.g. finite element methods, finite difference methods, etc. However, it seems difficult and time-consuming for the modeling and mesh generation of multiscale microstructure of cement paste. Besides, calculations in these models usually require a lot of computing resources and sometimes are hard to achieve convergence, which may result in inaccurate results.

Fortunately, cement paste is a typical fractal material and its pore structure exhibits obvious self-similar fractal features [20]. Fractal models have been developed to investigate transport properties of porous media on the basis of their fractal features [21–23]. It has been extensively validated that the utilization of fractal models for transport property analysis are efficient and reliable [24–26]. However, how to identify fractal features of porous media is a big challenge, which limits the application of fractal models. In most of previous studies, fractal features of porous media are detected by either image analysis techniques e.g. small angle X-ray scattering (SAXS) [27], scanning electron microscopy (SEM) [28], computed tomography (CT) scan [29,30] or pore network analysis via experimental tests [31,32]. However, these methods always require complex specimen preparations and test procedures.

This work aims to present a feasible computer simulation to predict the evolution of microstructure and transport properties of cement paste with acceptable accuracy and computing time. Firstly, a computer-based simulation associated with the microstructure of cement paste is constructed. In this simulation, volume of each constituent phases of cement paste can be calculated based on the given volume stoichiometry factor (k_h), water to cement ratio (w/c) and hydration degree (α). Simulation algorithm is illustrated in detail and proved to be efficient. Simulated results are comprehensively analyzed, and verified with those from experimental tests and other simulations. Then, fractal features of cement paste are directly obtained through the simulated microstructure. The evolution of fractal features with porosity is verified by literature results. Finally, fractal models are adopted to predict transport properties of cement paste, including permeability, diffusivity, and thermal conductivity. The evolution of transport properties with age, hydration degree and porosity is comprehensively analyzed. For the verification of fractal models, experimental data and results from other models in literature are adopted to make comparisons.

2. Constituent phases and pore structure of cement paste

Along with the hydration, cement grains gradually dissolve and a porous shell of hydrated products form around each grain. Generally speaking, a hydrated cement paste often consists of three constituent phases, i.e., unhydrated cement grains, hydrated products, and pore phases that were originally occupied by water. Hydrated products in cement paste generally consist of calcium silicate hydrate (CSH) gels and hydrated crystals including calcium hydroxide (CH), monosulfate (AFm) and ettringite (AFt). It is reported that the main hydrated products are CSH gels and CH, where CSH gels make up approximately 70% of the total volume of hydrated products [33]. With regard to pore structure, it is suggested that pores in cement paste should be divided into gel and capillary pores [34]. Gel pores intrinsically locate inside CSH gels with size from serval nanometers to about 10 nm. Capillary pores have the size from 10 nm to tens of micrometers and are considered as the remnants of the initially water-filled space. Capillary pores can be further divided into small capillary pores (10–100 nm) and large capillary pores (>100 nm) [3].

Based on previous research [35], a three-level representation of multiscale microstructure of cement paste is illustrated in Fig. 1.

Level 0: Nanoscale - nano pores

In the three-scale level model established in this work, Level 0 illustrates the basic building block of CSH gel, namely the CSH solid. Jennings provided sufficient evidence of an amorphous colloidal structure of CSH gel, organized in "globules", composed of basic building blocks and intra-globules porosity [35,36]. At this scale, porosity is intrinsic to CSH solid and referred to as nanoporosity filled by structural water.

Level 1: CSH gels - gel pores

According to previous findings [35,36], CSH gel is a component of CSH solid, interlayer space, intra-globule space, and monolayer water. It is well established that CSH gels exhibit low and high-density forms, due to their different packing configurations: gel porosity of roughly 24% for HD CSH, and 37% for LD CSH. It is noted that LD CSH tends to form at the very beginning of hydration since there is enough pore space in cement paste [35,36]. As hydrated products gradually precipitate and accumulate, the pore space becomes small and the formation of hydrated products is restrained, leading to the possible transformation from LD CSH to HD CSH [37].

Level 2: CSH foams - small capillary pores

Hydrated crystals usually have nano and micro scales, which can be distinguished by SEM test [38]. Besides, micromechanical analyses show that CSH and hydrated crystals are associated not merely as a simple mixture, but as an intimate nanocomposite [38]. Nanoscale hydrated crystals reinforce CSH by partially filling gel pores in CSH, which indicates that nanoscale hydrated crystals grow in a restrained state. In capillary pores, hydrated crystals can nucleate and grow continuously to be microscale [39]. In order to simulate the complex intersection of hydrated products, two kinds of CSH foams are constructed in this work to represent the configuration of CSH/crystal nanocomposite. Level 2 illustrates the construction of CSH foams at the length scale of 10^{-7}–10^{-6} m. HD CSH foam is considered as a mixture of HD CSH and nanoscale hydrated crystals, and LD CSH foam contains LD CSH, nanoscale hydrated crystals and small capillary pores.

Level 3: cement paste - large capillary pores

Level 3 illustrates cement paste at a characteristic length scale of 10^{-6}–10^{-4} m. At this scale, unhydrated cement grains together with CSH foams, visible hydrated crystals and large capillary pores are included in cement paste. As shown in Fig. 1, regions with color