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Two-scale modeling of the capillary network in hydrated cement paste

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HIGHLIGHTS

- Capillary pore network in hydrated cement paste is modeled at two different scales.
- Two status-oriented computer models are developed for the simulation works.
- The simulation methods are validated by appropriate experimental results.

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ABSTRACT

Objective: Studies on pore structure are essential to better understand the transport properties and durability of cement based materials. In this study, a two-scale modeling framework is proposed to simulate the capillary pore network in hydrated cement paste.

Methods: Capillary pores are divided into small capillary pores (SCPs) and large capillary pores (LCPs). It is assumed that all SCPs are embedded in the outer calcium silicate hydrates (C–S–H) layer, which is the mixture of low density (LD) C–S–H and SCPs at sub-micro-scale. The porosity of outer C–S–H layers is found to be a function of the water-to-cement ratio (*w/c*) and the degree of hydration. Using this porosity to define the status, the outer C–S–H layer is simulated as a two-phase mixture based on a sub-micro-scale status-oriented model. Using the degree of hydration to define the status of a cement paste, cement paste is simulated as a mixture of unhydrated cement cores, inner hydration products, outer C–S–H layers, micro-sized crystal hydrates particles and large capillary pores, based on a micro-scale status-oriented model.

Results: The two computer models developed for pore structure simulations of cement paste, at different scales, are verified by nitrogen adsorption and microscopic image processing, respectively.

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1. Introduction

Concrete is a fairly complex heterogeneous composite, with random microstructures at different length scales ranging from the microscopic nanometer scale to the macroscopic decimeter scale, over 9 orders of magnitude [1]. Even when cement paste is considered, its microstructural characteristics cover length scales of over 6 orders of magnitude. Due to this reason, no experimental approach or model alone is capable of fully revealing the microstructure of concrete/cement paste. According to the multi-scale system proposed by Wittmann [2], cement paste at the micro-level is the lowest level of concern for modeling concrete properties. Later developments in concrete science and technology led to efforts in investigations at lower level, i.e. nano-level [3,4]. At the nano-level, C–S–H (calcium silicate hydrates) may be described as short-ordered structures, and atomistic/molecular dynamics simulations can be employed to get insights in the structure on the basis of tobermorite and jennite crystals. Recently, it has been recognized that the geometrical gap between the micro- and the nano-level is too large. Thus, a sub-micro-level should be inserted between micro- and nano-level, where the colloidal or gel-like properties of C–S–H can be studied [5], in light of the colloidal models [6–11].

In the microstructure of concrete, capillary pores have always attracted attention from researchers, as they have strong relationship with the transport properties of concrete, which govern the durability of concrete structures to a large extent [12]. The size of capillary pores can be from less than 10 nm to larger than 10 μm, spanning over 4–5 orders of magnitude. Such a multi-scale nature makes it difficult to characterize capillary pores using one technique or one model. In most of the existing computer models, such as DuCOM [12,13], CEMHYD3D [14,15], HYMOSTRUC [16–18] and μic [19], the capillary pore network seems to be simply simulated as one phase of cement paste at the micro-scale. In this way,

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information on capillary pores at the sub-micro-level may be missing, or misleadingly obtained. However, if capillary pores are divided into different types and considered at different length scales, the capillary network may be simulated more realistically. In this study, a two-scale microstructural modeling framework, which mainly concerns a more realistic arrangement of capillary pores in cement paste, is developed. In light of previous work [20,21], capillary pores are divided into small capillary pores (SCPs, ~3–100 nm in diameter) and large capillary pores (LCPs, >100 nm in diameter), approximately corresponding to those parts of capillary pores that can be characterized by nitrogen adsorption [22] and those that can be detected by BSE (Back-scattered Scanning Electron microscopy) [23], respectively. SCP and LCP networks are simulated respectively at the sub-micro-level and micro-level by two different computer models, and validated appropriately. It is interesting to note that the 100 nm, which is used to divide capillary pores into two categories in the present study, was also considered as a critical pore size in classic works. Wu and Lian [24] classified pores larger than 100 nm as harmful pores while those smaller as little-harmful and harmless pores as far as durability and mechanical properties of concrete are considered. Mehta and Monteiro [25] pointed out that in hydrated cement paste, a direct relationship can be shown between the permeability and the volume of pores larger than about 100 nm, because when most of pores are reduced in size to 100 nm or less, they lose their interconnections.

2. Microstructure description and modeling strategy

2.1. Basic simplifications of the microstructure of cement paste

In light of BSE, the capillary pore geometry can be observed, but the porosity detected is lower than that measured by MIP (Mercury Intrusion Porosimetry), or calculated from Powers' model [20]. This is because this technique cannot cover the whole pore size range. Balancing the resolution and the representability, the smallest pore size that can be detected by BSE is normally limited to 100–400 nm [23]. Nitrogen adsorption based BJH method [26], which characterizes small capillary pores from several to 100 nm [22], seems to be complementary to the BSE method to cover the whole size range of capillary pores [20]. On a BSE image, due to the principles of BSE imaging [27], some pixels which in fact contain solid intermixed with small pores (smaller than the pixel size) are defined as pores, and some in which the ratio of solid to pores is somewhat higher are defined as solid. The latter case should occur much more frequently than the former, as the volume fraction of hydrate solids is much larger than that of small capillary pores [20]. Thus, small capillary pores should actually exist in the hydrate phases on a BSE image. This discussion leads to reasonable assumptions as follows:

(1) At the micro-level, corresponding to the morphology as observed under BSE, cement paste consists of unhydrated cement cores (mineral clinker), inner hydration products layers, outer hydration products layers (outer C–S–H layers and crystal hydrates particles) and large capillary pores, as shown in Fig. 1; inner hydration products include high density (HD) C–S–H and small (nano-sized) particles of crystal hydrates such as calcium hydroxide and aluminate hydrates [28], while the outer hydration products include low density (LD) C–S–H and large (micro-sized) particles of crystal hydrates.
(2) Small capillary pores out of the detectable range of BSE, as characterized by the nitrogen adsorption method, are assumed to be embedded in the outer C–S–H layers, as shown in Fig. 1. It might be the mixtures of small capillary pores and LD C–S–H which actually contribute to the lower density C–S–H types defined by nano-indentation [28,29], as nano-indentation does not distinguish capillary pores in this range from C–S–H.

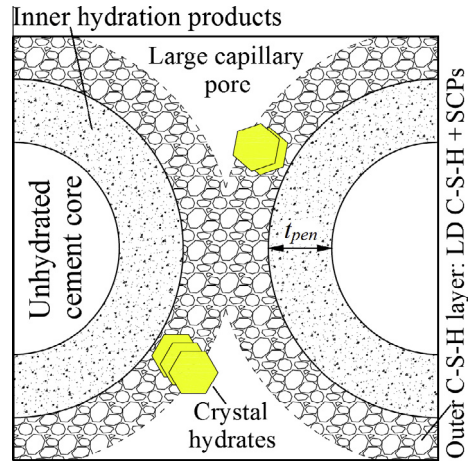

Fig. 1. Sketch map of the basic simplifications.

2.2. Micro-structural characteristics and length-scale division

It has been accepted generally that C–S–H is nano-crystalline in small local regions, and it has a layered (e.g. foil-like) structure [7–9,30–32]. However, the way in which these small local regions are arranged together is not yet understood. The most likely way, as has been proven by experiments, is that C–S–H gel is composed of colloidal particles with irregular shape but comparable volume. The layered (crystalline) structure inside the C–S–H particles is generally simulated in light of molecular dynamics based on tobermorite and jennite crystals [3,4], at the scale of 10^{-10}–10^{-9} m. Detailed discussion of such structures means a lot in modeling mechanical properties, as it is the largest scale at which mechanical properties do not change from one sample to another. However, it means little for modeling transport properties as the pore space at this scale is comparable with the size of the main migrating ions/molecules in cement based materials. The smallest micro-structural characteristics that need to be concerned when modeling transport properties of cement based materials are LD C–S–H and HD C–S–H, as defined by Jennings [7–9]. The microstructure of cement paste, when related to transport properties, can be discussed at three different scales:

(1) *C–S–H gel:* This is a nano-level (10^{-9}–10^{-7} m), although it is higher level than the nano-level defined by others [3]. At this length scale, LD C–S–H and HD C–S–H are distinguished and can be modeled based on the colloidal models [6–11,33].
(2) *Hydration products layers:* This is a sub-micro-scale ($<10^{-6}$ m), at which the inner hydration products layer can be considered as a mixture of HD C–S–H and nano-sized crystal hydrates particles, and strictly it should also contain inert cement residue. An outer products layer is a mixture of LD C–S–H, small capillary pores (from several to 100 nm in diameter) and large (micro-sized) crystal hydrates particles. As large crystal hydrates particles, e.g. calcium hydroxide, ettringite and AFm phases, are normally of micron size, they should be considered as microstructural characteristics at a higher level, so that the remaining part of the outer hydration products layer can be treated as a mixture of LD C–S–H and small capillary pores, and named the outer C–S–H layer.

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