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Effective diffusivity of cement pastes from virtual microstructures: Role of gel porosity and capillary pore percolation

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HIGHLIGHTS

- The percolation threshold at around 20% of capillary porosity required for correct predictions.
- Differences between diffusivity obtained from different techniques due to difference in contribution of gel pores.
- Constrictivity parameter for C-S-H is 1/10.

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ABSTRACT

The role of capillary pores percolation and gel pores are investigated to explain the underlying differences between relative diffusivity obtained from different experimental techniques using microstructures generated from two different types of hydration model viz., CEMHYD3D (a voxel based approach) and HYMOSTRUC (a vector based approach). These models provide microstructures with different capillary pore connectivity for the same degree of hydration and the same porosity due to the underlying assumptions. In order to account for a C-S-H diffusivity at the micro-scale, a continuum micro-mechanics based model has been proposed. These simulations show that deperolation of capillary pores at around 20% of capillary porosity is essential in order to correctly predict diffusivity of cement paste with water-cement ratio by mass (w/c) in between 0.4 and 0.5. Furthermore from our analysis we present a viable postulate that the higher diffusivity measured by electric resistivity compared to other methods is due to differences in contribution from gel pores. For electrical resistivity measurement it is proposed that all gel pores are diffusive whereas for ion and tracer transport it is proposed that only nitrogen accessible gel pores are diffusive.

1. Introduction

Diffusivity is a crucial parameter to assess the impact of several deterioration mechanisms such as sulphate attack, leaching, carbonation, chloride transport for coastal concrete structures, and to predict contaminant transport in cementitious barriers in hazardous waste disposal systems. It is also used as a key durability indicator to define the service life of concrete structures. Diffusivity is closely related to the morphological features of concrete which exhibits a complex multi-scale nature [1]. Morphological heterogeneities of concrete from modeling point of view can be conceptually divided into different material scales as shown in Fig. 1 viz., macro-, meso-, micro-, sub-micro- and nano-scales [1]. At the macro-scale cementitious material is treated as continuum; at meso-scale, aggregates, interface transition zone (ITZ) and cement paste are explicitly represented; at micro-scale heterogenities at the cement paste are represented however C-S-H phase is treated as a continuum; heterogeneities in the C-S-H phase are resolved at sub-micro- and nano-scales. It has been shown by recent compilation of experimental data on mortar and concrete diffusivity by Patel et al. [2] and through numerical modeling by Bentz et al. [3], that the contribution of ITZ to diffusivity is negligible. Consequently, diffusivity can be described solely in terms of the volume fractions of aggregates and cement paste. Patel et al. [2] also reported that different experimental techniques result in differences in the values of relative diffusivity of cementitous

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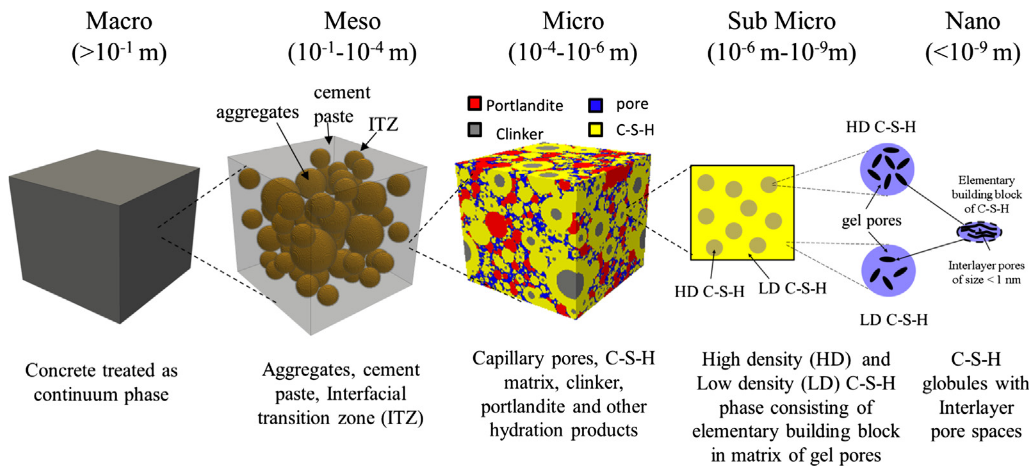

Fig. 1. Multi-scale representation of morphological heterogeneities of concrete from modeller's view point.

materials (relative diffusivity is the ratio of effective diffusivity of a porous medium to that of the tracer in water). Especially, diffusivities obtained from electric resistivity experiments are higher compared to those from other techniques. Differences are more prominent at lower water-cement ratio (w/c) and mainly manifests at the micro- and lower scales which cannot be explained using existing analytical models based on effective media theory. As, at these scales diffusion occurs mainly through gel and capillary pores, one needs to understand and differentiate the influence of gel pores and capillary pores connectivity on diffusivity to explain the discrepancies between different experimental results.

In this study, cement paste morphology is generated using three dimensional hydration models to better understand the role of gel pores and capillary pores connectivity on diffusivity. These hydration models can be classified as suggested by Thomas et al. [4] based on the conceptual assumptions used for representing the cement particles into vector based models (e.g. HYMOSTRUC [5–8] and μic [9]) and voxel based models (e.g. CEMHYD3D [10,11] and HydratiCA [12]). These hydration models have been calibrated to obtain the evolution of the microstructure and morphology taking into account the reactions at the cement particle level as a starting point, and considering the effects of particle size distribution, chemical composition of cement paste, water-cement ratio by mass (w/c) and curing on hydration. However, the simulated cement paste morphology differ substantially between different hydration models for the same volume fraction of hydration products and capillary porosity. For example, the capillary pore deprcolation occurs at around 5% [13] and 18 to 20% [14,15] for HYMOSTRUC and CEMHYD3D generated microstructures, respectively (irrespective of w/c ratio) for 1 μm resolution. Thus, for the same capillary porosity one can achieve different connectivity from these models. Therefore in this study utilizing both CEMHYD3D (available in VCCTL software [16]) and HYMOSTRUC (modified version which includes nucleation and growth of portlandite [8]) allows us to investigate the role of capillary pore percolation.

At the micro-scale, the C-S-H phase containing sub-micro- and nano-scale porosity, i.e., gel porosity is treated as a continuum media due to the limitation of resolution within the simulation. However,diffusivity of the C-S-H phase is very difficult to measure and is often fitted by calibration of models using experimental data of cement paste. For virtual microstructures generated from CEMHYD3D, Garboczi and Bentz [17] suggested value 0.0025 for the relative diffusivity of C-S-H based on the calibration using steady state chloride ion diffusion experiments of [18,19]. These experiments were carried out for w/c ratios in the range of 0.3–0.7. Bentz et al. [20] using this value for C-S-H diffusivity and CEMHYD3D generated microstructures showed that good predictions (within factor 2 bounds) can be achieved for cement paste diffusivity even for the low w/c ratio. Bentz et al. [21] using overlapping sphere models from C-S-H and assuming that the transport occurs only through cluster level pores computed relative diffusivity of 0.0033. Kamali-Bernard et al. [22] obtained a value of 0.001 for the relative diffusivity of C-S-H by fitting diffusivity obtained using CEMHYD3D microstructures to the experimental data of [23] at a w/c ratio of 0.25. Ma et al. [24] proposed the value of 0.00775 for the relative diffusivity of the C-S-H phase based on electric conductivity measurements using the diffusion model of Oh and Jang [25]. Recently, Ma et al. [26] developed a two-scale approach to determine the diffusivity of cement paste from virtual microstructures. The microstructure of cement paste is generated using a vector based approach analogous to HYMOSTRUC. The diffusivity of C-S-H phase was determined considering that transport occurs only through low density (LD) C-S-H which is simulated using a modified hard-cores/soft shell model. On comparison with the experimental data for electric resistivity they observed that their predictions do not comply well at later stage of hydration and for low w/c. Thus there is no general consensus on a unilateral value of C-S-H diffusivity. Therefore in this study, a continuum micromechanics based model to predict diffusivity of C-S-H phase has been proposed which predicts diffusivity of C-S-H considering its morphological features. Finally, diffusivity of cement paste is estimated from virtual microstructure using lattice Boltzmann method wherein C-S-H phase is treated as a continuum phase with diffusivity value assigned using the proposed C-S-H diffusion model. Predictions are compared to data obtained from different experimental techniques to understand the role of gel pores and capillary pore connectivity on diffusivity of cement paste. The remainder of the paper is organized as follow. Section 2 presents the modelling approach wherein the governing equations for the computational homogenization approach to obtain the diffusivity from virtual microstructures are first presented. Following that a C-S-H diffusivity model is introduced. Section 3 compares experimental results and model predictions and discusses the roles of gel and capillary porosity in different types of experiments. Finally, conclusions are presented in Section 4.

2. Determination of effective diffusion coefficient from virtual microstructures

2.1. Computational homogenization approach to determine diffusivity

At the scale of cement paste microstructures, the computational domain consists of capillary pores (Ω_p), porous C-S-H phase (Ω_{CSH})