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Modelling of diffusion behavior of ions in low-density and high-density calcium silicate hydrate

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HIGHLIGHTS

- The relationship between morphology and specific ion diffusion behavior in LD and HD C-S-H is determined.
- 3D C-S-H structures are generated with a muitiscale method.
- Effects of electrical double layer on ion diffusion in C-S-H is introduced and quantified.
- Diffuse layer promotes counterion diffusivity but retards conion diffusivity.
- Diffusivities in hardened cement pastes are predicted using modelling diffusivities in LD and HD C-S-H.

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ABSTRACT

To investigate the relationship between morphology and specific ion transport properties in low-density (LD) and high-density (HD) calcium-silicate-hydrate (C-S-H), a numerical method of directly achieving diffusivities is developed. Firstly, a multiscale structural model is proposed to reconstruct C-S-Hs in which self-similarity and quantitative physical properties are compared to experimental results. Subsequently, electrical double layer (EDL) theory is introduced into analysis of ion transport in pore solution. The quantitative analysis of various influence factors of EDL on ion diffusivities in pore solution is carried out and average diffusivity in pore solution is also obtained. Moreover, a numerical method for solving Fick's first law equation is performed on the simulated C-S-H structures to obtain numerous diffusivities of common ions in C-S-H. Finally, the significant parameter for durability in reinforcement concrete, chloride diffusivity in hardened cement paste, is predicted using simulated diffusivities in C-S-Hs, based on a multiscale method. It is found that compared to the atomic force microscope image and surface area of C-S-H, this self-similar model can well reconstruct real C-S-H structures. In addition, the influence factors of EDL including overlapping diffuse layer, relative potential, cation/anion, valence, zeta potential and bulk solution have great effects on ion diffusivities, which demonstrates EDL effects cannot be ignored when investigating ion transport behavior in C-S-H. Furthermore, using an appropriate case of pore solution with diffusivities of 8.2×10^{-12} m^2/s in LD C-S-H and 2.0×10^{-13} m^2/s in HD C-S-H, estimated chloride diffusivities in cement pastes agree well with measured values, which can indirectly indicate this modelling work is reasonable.

1. Introduction

The phenomenon of ions migrating from service environment into concrete, then inducing steel bar corrosion, sulfate attack, etc, is the source of durability problems in cementitious materials[1,2]. Ion transport rate in cementitious materials strongly depends on characteristics of pore phases [3–5], while the transport control mechanisms are different at various pore structure states. With cement particles hydrating, connected capillary pore as fast transport access of ions at early time in cement paste is gradually filled and blocked by hydration products. Eventually, ion transport rate in porous calcium silicate hydrate (C-S-H) will play a decisive role in transport rate in cement-based bulk [6]. Therefore, understanding the nature of ion transport behavior in C-S-H is of significance for studying durability and predicting service life in cement-based materials.

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In the past few decades, many advanced characterization techniques have been utilized to investigate the structure of main hydration product – C-S-H. From atomic force microscope (AFM) investigation [7], small angel neutron scattering (SANS) [8] and transmission electron microcopy (TEM) [9], there is ample evidence that the elementary C-S-H particle is a nanoparticle with size of on the order of 5 nm. Based on different gel porosity obtained from different types and modes of observation, C-S-H consisting of these nanoparticles is divided into low-density (LD) C-S-H (outer product) and high-density (HD) C-S-H (inner product) [7–12]. Although a large amount of breakthrough has been acquired in understanding the structure of C-S-H, the accurate fundamental parameters of C-S-H are still in ambiguity such as gel pore size distribution.

In terms of transport properties in C-S-H, the diffusivity in C-S-H was obtained by the inversions of modelling or experimental data in hardened cement paste [6,13–17] or molecular dynamics studies in nanoscale [18–20]. Bentz and Garbociz [6,13] proposed the relative diffusivity in C-S-H was 0.0025–0.0033 based on CEMHYD3D model of simulating cement hydration and microstructural development. Coverdale et al. [14] modified this relative diffusivity into an approximate value of 0.01 by fitting simulated values to measured results. Liu et al. [15] used the general effective media (GEM) model to deduce the relative diffusivity of C-S-H to be 0.0083. Recently, many literatures [16,17] reported tritiated water (HTO) diffusion coefficient in LD C-S-H was from 3.4×10^{-12} m^2/s to 9.0×10^{-12} m^2/s and that in HD C-S-H was between 1.0×10^{-13} and 8.3×10^{-13} m^2/s according to experimental results and analytical model. These results can give a good understanding for overall (relative) diffusivity in C-S-H, however, the diffusion rates in the same materials between specific ions may have a wide gap due to their own different features [21] and electrical double layer (EDL) [22]. For example, anion and cation diffusion coefficients in cementitious materials may differ by an order of magnitude in diffusion cell experiments [23,24]. Goto et al. [23] even reported Cl^- diffusivity was 612 times greater than Na^+diffusivity in hardened cement paste with water-to-cement ratio (w/c) of 0.4. Alternatively, many studies [18–20] devoted to using molecular dynamics calculation based on the force field to investigate ion transport behavior in molecular scale. However, these studies mainly focused on the effect of its structure (jennite and tobermorite), Ca/Si ratios, pore solution etc, on ion or water diffusive behavior in a local gel pore without considering complicated gel pore structure. Consequently, it is urgent to investigate specific ion transport behavior in C-S-H in sub-microscale to bind that in molecular scale and microscale, which is of great significance for service life prediction and nuclear waste stabilization in cement-based materials.

Due to observation of disparate cation and anion diffusivities combined with measurement of significantly high membrane potentials and zeta potentials in cementitious materials [25–28], Chaterji and Kawamura [24,29] proposed EDL may serve as the underlying cause of this phenomenon. During the past century, EDL model witnessed its own development and consummation including Helmholtz model, Gouy-Chapman model, Grahame model and Stern model [30] and since that time, numerous studies have aimed at illustrating manifestations of EDL in various materials. In recent years, many investigations gradually concentrated on the quantitative calculation of the influence of EDL on ion transport in cementitious materials. Fridemann et al. [31] described the effects of EDL on ion transport in a simply pore geometry under the condition of pore solution with a symmetric electrolyte composition. On the basis of these assumptions, Arnold et al. [22] used solution of nonlinear Poisson-Boltzmann equation to study this effect on ion transport in pores with real pore size distribution and on different ion concentration distribution in a "necking" pore. Recently, He et al. [32] investigated relationship between chloride ion concentration of expressed pore solution and exposure solution of cementitious materials exposed to a chloride salt solution. Unfortunately, due to the complexity of cementitious materials in both composition and pore morphology, this phenomenon still need to continue in-deep investigation.

This study aims at developing a numerical model to address the question of the relationship between morphology and ion transport properties in LD and HD C-S-H. For the purpose of numerical calculation of ion diffusivities, we firstly propose a self-similar multiscale structure model of C-S-H and present some methods to perform a quantitative analysis on gel pore size and connectivity in two C-S-Hs. The next section focuses on quantitatively calculating the effects of EDL on ion diffusion behavior in pore solution in C-S-Hs. The influence factors include overlapping diffuse layer, relative potential, cation/anion, valence, zeta potential, bulk solution, etc. The average ion diffusivities in pore solution based on pore size distribution of real C-S-H gel measured from experiments are used to validate the accuracy of modelling results based on pore size distribution of self-similar C-S-H structure. In the third section, a numerical approach to solving diffusion control equation is developed for obtaining ion diffusion coefficients in LD and HD C-S-H, considering the influence of EDL and pore morphology on ion transport behavior. Numerous diffusivities of common ions in C-S-Hs are predicted. Finally, due to the crucial role of chloride diffusivities in durability and service life prediction in cement-based materials, the obtained chloride diffusivities in LD and HD C-S-H are applied to predict diffusivities in hardened cement pastes with various w/cs generated using CEMHYD3D model. In additional, by means of a comparison to a large amount of experimental data in hardened cement pastes, simulated diffusivities in C-S-Hs are also indirectly validated.

2. Modelling

2.1. Structures of C-S-Hs

LD and HD C-S-H are made up of different structures with total porosities of 36% and 26% packed with a wealth of around 5 nm nanoparticles [8]. Furthermore, colloid model [8,10] demonstrated that these nanoparticles pack into a fractal structure and the same volume fractal region will gradually grow into larger and self-similar C-S-H structures. As such, these grown C-S-Hs are uniform structures but with different packing densities. In order to carry out modelling work, we choose 5 nm spherical particles as minimum packing elements and employ them to construct different morphologies of LD and HD C-S-H based on a hard core-soft shell (HCSS) algorithm in a cubic representative volume element (RVE) [13,33,34]. Herein, HCSS algorithm in C-S-H structure model means each individual C-S-H particle consists of an impenetrable hard core surrounded by a concentric soft shell. During packing process, the soft shell of a new introduced C-S-H nanoparticle can overlap freely with soft shells and hard cores of other particles in RVE, but the hard core of this new nanoparticle can only overlap with existing soft shells.

On the other hand, since uniform C-S-H structure contains multi-size pores from a few nanometers to dozens of ones (close to capillary pore size), the pore heterogeneity at different scales cannot be investigated in one scale. To overcome this conundrum, Bentz et al. [33] firstly proposed a multi-scale model of C-S-H structure based on real TEM images of C-S-H to study dry shrinkage of cement paste, namely micro-level and macro-level C-S-H. Nevertheless, C-S-H has a total porosity of 28.2% in their study, which cannot explain later presented structures of LD and HD C-S-H with porosities of 26% and 36% respectively. Consequently,