



Molecular dynamics study on the chemical bound, physical adsorbed and ultra-confined water molecules in the nano-pore of calcium silicate hydrate



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HIGHLIGHTS

- Surface water shows higher dipole moment due to hydrophilic C-S-H layers.
- The mobility of interlayer water, hydroxyl is reduced greatly due to H-bond restriction.
- The oxygen in defective silicate chains influences water orientation and packing behavior.
- Surface Ca ions and OH groups are dissociated from the C-S-H surface.

ARTICLE INFO

Article history:

Received 28 February 2017

Received in revised form 25 May 2017

Accepted 10 June 2017

Keywords:

Molecular dynamics
Calcium silicate hydrate
H-bonds

ABSTRACT

The movement of water molecules confined in the calcium silicate hydrate gel determines the chemical and physical properties of cement-based materials. In this paper, the molecular dynamics was utilized to investigate the structure and dynamic properties of interlayer water, surface adsorbed water and the capillary water molecules. The molecular structure of water molecule ultra-confined in the C-S-H gel or in the vicinity of calcium silicate surface is changed dramatically as compared with capillary water: enlargement of packing intensity, increasing magnitude of dipole moment, enhancement of the order interfacial organization, improvement of orientation preference and the extending of water-water spatial correlation. These structural features are attributed to the hydrophilic nature of the C-S-H surface that can provide non-bridging oxygen atoms in the silicate chains to accept H-bonds from the surface adsorbed water molecules and highly solvated calcium atoms in the interlayer region to associate confined water molecule to form hydration shell. Furthermore, three types of water molecules can be clearly distinguished by the diffusion coefficient derived from the mean square displacement of water molecules: Interlayer water ($0.003 \times 10^{-9} \text{m}^2 \text{s}^{-1}$) \ll surface water ($1.2 \times 10^{-9} \text{m}^2 \text{s}^{-1}$) $<$ capillary water ($2 \times 10^{-9} \text{m}^2 \text{s}^{-1}$). The slow dynamic properties of interlayer water resemble that in the glassy state: water molecules are hard to escape from the “cage” constructed by the H-bonds and ionic bonds network.

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1. Introduction

Concrete is the most widely utilized construction and building materials all over the world. The cement paste, binding phase in the concrete materials, determines the mechanical properties and durability of the material [1]. In the cement-based material, calcium silicate hydrate (C-S-H) is the main hydration product, which takes account of nearly 70% of the volume of the total products and plays essential role in the strength development of the material [2].

The C-S-H gel has micro- and meso-porous structures that include the solid ordered-disordered calcium silicate skeletons with ions and water molecules confined between different layers. The movement of water molecules has great influence on various physical and chemical properties of C-S-H gel, which further determine the macro-scale behavior of cement-based materials such as creep, shrinkage and reactivity [3–5]. For example, water molecules can carry chloride ions and other detrimental ions through the porous cement hydrate, which causes the corrosion of reinforcement and damage of the concrete structure [6–8].

The properties of the water confined in gel pore or in the vicinity of C-S-H surface have been studied by various experimental techniques. According to Mindess et al. most cements will

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completely hydrate at long hydration times when the ratio of water to cement is 0.42 [9]. As the cement reacts with the water it forms chemically bound water either in C-S-H or a calcium sulphate aluminate phase or calcium hydroxide. The remaining water will be in either capillary or gel pores [10]. Bordallo et al. carried out a series of quasi-elastic neutron scattering (QENS) experiments and differentiated between three different water interactions: chemically bound water that reacted with cement, physically bound water that interacted with the surface of the gel pore in the paste and unbound water that was confined in the larger capillary pores. And diffusive motion was characterized by diffusion constants in the range of $(0.6\text{--}2) \cdot 10^{-9} \text{ m}^2/\text{s}$, which is much smaller than the diffusion constant of bulk water [11]. In addition, the reaction details of water with C_3S and the diffusion coefficient of water molecules were also investigated by QENS [12]. And the diffusion coefficient was consistent with the value obtained from ^1H NMR [13,14]. Based on proton magnetic relaxation dispersion (NMRD), Korbet al. have proposed a direct method of surface dynamics of various cement-based materials. This technique can clearly distinguish the movement of water at the surface of the pores and the bulk water [15]. Although the experimental study of water molecules has made some progress, but the water molecules in the nano-pores in physical and chemical changes have not been completely understood, it must be based on nano-scale molecular dynamics simulation. Molecular dynamics, a force field based on computational method, is able to give a more quantitative illustration on the structure, dynamics and energy of solid-liquid interfaces.

By using molecular dynamics, Hou et al. studied the water and ions transported in silt-shape nanometer pore constructed by the mineral analogue of calcium silicate hydrate gel, tobermorite and jennite [16,17]. They investigated the dynamics and structure of confined water by analyzing H-bond network, diffusion coefficient and so on. However, the crystal structure of tobermorite and jennite cannot completely represent the C-S-H, because there are plenty of discrepancies between C-S-H gel and the mineral analogues such as the Ca/Si ratio, density and water content [18,19]. P.A. Bonuaud et al. investigated the thermodynamics of water confined in porous of C-S-H. They proved that the surface of C-S-H was highly hydrophilic because they observed that above 20% RH all nanometer-scale cement pores were filled with water. Moreover, they found that water molecules lead to a disjoining behavior inside the C-S-H grain. And the cohesion originated chiefly from the calcium ions that interact strongly with the C-S-H substrate [20]. Based on empirical force field molecular simulation, Yousef et al. demonstrated that the C-S-H gel pore was hydrophilic and the confined water in C-S-H had a multi-characteristic structure on multi-range. More importantly, they proposed that the dynamics properties of ultra-confined water molecules in the disordered calcium silicate layers resemble of that of super-cooled liquid or glass [21]. Based on 150 different models M.J. Qomi et al. found that the motion of confined water shows a multi-stage dynamics which is characteristic of supercooled liquids and glassy phases and the mobility of water molecules is composition – dependent [22]. Manzano et al. used the ReaxFF force field to show that water does dissociate to form hydroxyl groups and analyze the water dissociation mechanism. Finally, they established a relationship between water dissociation in C-S-H gel and the increase of hardness due to a transformation from a two- to a three-dimensional structure [23].

Above all, many works have been done about C-S-H gel and mineral analog of C-S-H. Beyond that, the transport of water through high aspect ratio hourglass-shaped pore has been investigated [24]. But the transportation of water confined in C-S-H gel pore, specially, in relatively large gel pore has been rarely studied. In this paper, we employed molecular dynamics method to study

the water transport in C-S-H gel pore. The C-S-H model proposed by Hou et al. [25] was utilized as the substrates of the nanometer pore. The molecular structure and dynamics properties of water molecules transport in the gel pore were characterized by systematically analyzed the density profiles, radial distribution function (RDF), coordination number (CN), atomic trajectories, H-bond networks and diffusion coefficients. The geometric and electronic influence of the disordered calcium silicate substrate is further discussed by studying the structural and dynamics evolution of confined water molecules.

2. Computational method

2.1. Force field

In our simulation, the ClayFF force field, developed by Cygan et al., was utilized to calculate the interaction between different atoms, including water solution and the cement-related phases. The parameters of the force field can be found in literature [26]. It has been confirmed that ClayFF force field can accurately describe clay, hydroxide, and oxyhydroxide phases and their interfaces with aqueous solutions [27,28]. Furthermore, The complex structures related with cement-based materials, including tobermorite, layered double hydroxides, were successfully simulated by ClayFF force field [29,30]. Therefore, due to the similarity of the structure and components, it is suitable for the ClayFF force field to describe the simulation.

2.2. Simulation model

The C-S-H model with Ca/Si ratio of 1.7 proposed by Hou et al. [25] was taken as the initial structure of C-S-H gel substrate. The model has been validated by experimental data, such as XRD, NMR and SANS [18,31,32]. The chemical composition of the model is $\text{C}_{1.65}\text{SiH}_{1.8}$, consistent with the SANS test. The mean silicate chain length ($\text{MCL} = 2(Q_2/Q_1 + 1)$) in this model is around 2.58 with $Q_1 = 73.9\%$, $Q_2 = 21.4\%$ and $Q_0 = 4.7\%$, which matches well with the experimental results from the NMR test. Furthermore, besides water molecules, the silicate hydroxyl and calcium hydroxyl groups are present in the interlayer region in the model. As shown in Fig. 1a, the unit cell contains 144 calcium atoms, 85 silicate atoms and 236 water molecules and hydroxyl groups. The dimensions are $a = 21.6 \text{ \AA}$, $b = 22.52 \text{ \AA}$, $c = 23.13 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. The supercell consists of $2 \times 2 \times 2$ unit cells and then the supercell is cut along the crystal structure at the center of interlayer region that is parallel to the (001) crystallographic plane. Accordingly, the Ca_w (calcium ion in the interlayer) is adsorbed on the surface of the defective silicate chains. Then the two C-S-H substrates are separated to make gel pore with 6 nm width which represents a relatively large gel pore (the size of gel pore is 0.5–10 nm). In order to reduce the size effect, we employ periodic boundary conditions in three dimensions.

After creating the basic structure of the C-S-H, 4100 water molecules are put into the gel pore and the number of water molecules is calculated to satisfy the density of bulk aqueous solution under ambient conditions ($\sim 1 \text{ g/cm}^3$). Initially, the water molecules are randomly placed in the pore. This model of the C-S-H gel pore filled with water molecules is shown in Fig. 1b. The width of pore is 6 nm including 4100 water molecules and the thickness of the both C-S-H substrates are about 1.5 nm. The size of this model and the location of the C-S-H surface in the Z direction are marked on the left side of the Fig. 1.

Lammps, a large scale molecule modeling package, was applied to run molecular dynamics [33]. The temperature was set to 300 K and time step was 1 fs. In addition, the Hoover Canonical ensemble

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