Insight on the sodium and chloride ions adsorption mechanism on the ettringite crystal: Structure, dynamics and interfacial interaction

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ABSTRACT

The adsorption of water and ions on ettringite crystal, an important hydration product in the cement material, is fundamental to the durability of cement-based material. In this study, molecular dynamics was utilized to investigate the molecular structure, dynamics and interfacial bonding for the water and ions in the vicinity of ettringite crystal surface. The aluminate octahedron and sulfate ions in the surface of ettringite provide plenty of oxygen sites to accept H-bond from the water molecules in the interfacial region. The highly solvated surface calcium ions can strongly attract the neighboring water as their coordinate atoms. The hydrophilic nature of the ettringite interface results in the dramatically different feature of the water molecules on the ettringite surface, such as high dipole moment, ordered organization, good orientation preference and slow diffusivity. Furthermore, with gradually increasing simulation time, the calcium ions, aluminate and sulfate species in the crystal surface diffuse into the solution, resulting in the dissolution of the ettringite crystal and disturbance of the ordered interfacial topology. The six-coordinated aluminum hydroxyl groups transform to the aluminate tetrahedron, as they dissolve in the solution. Additionally, the chloride and sodium ions have different adsorption mechanism on the crystal surface. While the sodium ions are associated with the oxygen atoms in aluminate octahedron and sulfate ions by Na–O ionic bond and immigrate into the inner region of the dissolved crystal, the chloride ions can form the ionic pairs with the calcium ions, accumulating to cluster in the outer layer region. As compared with the chloride adsorption, the ettringite crystal has better immobilization ability on the cation ions due to the stable Na–O connection with long resident time.

1. Introduction

Concrete is the most widely used building material in the world and its durability is the basis for determining the long-term serviceability of concrete structures. Cement hydration products are porous structures (pore size of 0.5–10 nm). In erosive environments, such as seawater, water carrying harmful ions slowly penetrates into the interior of concrete through these nano-holes [1,2]. Erosion of water molecules and harmful ions are the main cause of durability deterioration of concrete structures [3–6]. On the one hand, hazard ions, e.g. chloride, destroy the passive film of steel bars and accelerate the corrosion of steel bars [7,8]; On the other hand, water and ions react with the pore interface, leading to the microstructure deterioration of concrete materials [9–11]. Therefore, it is of great significance to investigate the diffusion mechanism of water and ions in the nanometer channel of concrete.

The composition of the cement hydration product is extremely complicated. Ettringite $(Ca_6[Al(OH)_6]_2[SO_4]_3 \cdot 26H_2O)$ is one of the most important hydration products in Portland cement (approximately 7% proportion) and sulphoaluminate cement (approximately 25% proportion) [12,13]. It is also the principal secondary hydration product of concrete subjected to sulfate attack. Ettringite not only provides early-age strength of hardened concrete, but also compensates for the early-age shrinkage of the cement matrix. However, the molecular structure of ettringite is unstable, and the surrounding environment, such as ion concentration, temperature and pH value, has a great influence on the formation of ettringite. In order to make good use of ettringite, many researchers have explored its formation and stability conditions [14,15].

Macroscopic experiments, as important research methods, have made great progress in exploring the transmission of water and ions in concrete materials. Researchers have used neutron imaging technology

to study the migration of water in cement-based materials and concrete. It broke through the non-transparency of concrete materials and enabled the visual tracking of water intrusion in concrete and the quantitative calculation of water [16]. The high resolution ^{29}Si, ^{23}Na, ^{133}Cs solid state NMR has been used to study the effect of sodium chloride and cesium chloride on the cement hydration product C-S-H [17]. Further research found that the C-S-H interface with low Ca/Si ratio has better adsorption and curing ability for cesium ions [18]. In addition, the stability of ettringite deteriorates at high chloride concentration and forms the chloride-substituted monosulfate aluminates [19]. Zibara found that ettringite partially decomposes and forms Friedel's salt at higher sodium chloride concentrations ($> 2.0 mol/L$). The microstructure of ettringite contains a large number of open channels, the structural flexibility of ettringite has been exploited to solidify lead, zinc, chromium and other heavy metal ions [20]. Experimental studies illustrated that hydration products of cement had certain adsorption effect on ions, and water molecules, the adsorption ions in turn affected the structure of the products. However, these macroscopic experiments cannot explain its adsorption mechanism fundamentally.

Molecular dynamics method plays an important role in verification and supplement of experimental results [21,22]. Bonnaud et al. studied the thermodynamic behavior of water confined in C-S-H gel pores and demonstrated that the surface of C-S-H is highly hydrophilic [23,24]. Molecular modeling methods have used to investigate the transport properties of water or ions in the nanopore channels of cement hydration products. It was found that, as compared with the free water solution, the water molecules at the interface possess the characteristics of high packing density, orientation preference and low diffusion coefficient. Besides, the interface had certain adsorption capacity of ions [25–29]. Zhou et al. studied the adsorption and transport properties of chloride ions on C-S-H gel and demonstrated that C-S-H gel with high Ca/Si ratios had better resistance to chloride ion attacking [30].

The transport and adsorption characteristics of water and ions in gel pores of many different cement hydration products have been researched by molecular dynamics methods [25,26,28,29,31]. However, there are few studies on the transport and adsorption of water and ions in the ettringite nanopore [32,33]. In this paper, an ettringite nanopore was constructed based on the ideal ettringite model, and then the transport of water and ions in the gel pores was simulated by molecular dynamics method. Because of the complexity of transport and adsorption of water and ions within the channel, a variety of analytical methods such as density distribution, dipole angle, coordination number, radial distribution function and mean square displacement are applied to explore the microscopic mechanism comprehensively.

2. Methodology

2.1. Model construction

In this paper, Lammps software was used to construct the ettringite channel. As shown in Fig. 1a, based on the established ettringite model, the supercell were created, and the middle part was cut perpendicular to [0 0 1], then a 4.8 nm wide gel channel was created by adjusting the upper and lower substrates [1,2]. The resulting model parameters are: a = 44.67 Å, b = 38.68 Å, c = 85.44 Å, α = 90°, β = 90°, γ = 90°. As shown in Fig. 1b, 35Na$^+$ and 35Cl$^-$ were randomly placed in the middle of the 4.8 nm channel, and water molecules were absorbed into the pore to achieve saturation (1 g/cm^3) by Monte Carlo method, and finally created a concentration of 0.7 mol/L NaCl solution environment [32,34–38]. By simulating the transport of water molecules and ions in the ettringite pores, the interaction mechanism with ettringite was explored. It is worth mentioning that the periodic boundary has been set in the simulation process in order to eliminate the statistical error caused by the size effect [25–29]. Fig. 1d and e shows the top view of the model and the detail of the channel interface, respectively. It can be seen that the ideal ettringite structure is composed of[Ca$_3$Al

(OH)$_6$12H$_2$O]$^{3+}$ column, SO$_4$$^{2-}$ and water. [Ca$_3$Al(OH)$_6$12H$_2$O]$^{3+}$ column is made up of [Al(OH)$_6$]$^{3-}$ octahedra and CaO$_8$ polyhedrons, alternately arranged in one direction. SO$_4$$^{2-}$ and water molecules are distributed uniformly in the interstices of the column. Taking the connection of surface calcium in ettringite as the boundary, the model is divided into the ettringite substrate and the solution, as shown in Fig. 1c.

2.2. Force field and MD modeling procedure

The ClayFF force field developed by Cygan et al. was utilized in our simulations, which has been successfully used to simulate the interaction of oxides and hydroxide surfaces with water molecules and ions [39,40]. Hou et al. used this force field to simulate the transport of water and various ions in the gel pores of C-S-H, revealing the interaction of water molecules with the interface as well as the adsorption mechanism of ions on the interface [25–28]. The interaction force in the ClayFF force field is mainly composed of four parts, namely Coulomb force, Van der Waals force, bond length expansion potential energy and bond angle distortion potential energy, as shown in Eqs. (1)–(5). The specific parameters are derived from cygan et al. [41].

$$E_{total} = E_{coul} + E_{VDW} + E_{bond\ stretch} + E_{angle\ bend} \tag{1}$$

$$E_{coul} = \frac{e^2}{4\pi_0} \frac{q_1 q_2}{r^2} \tag{2}$$

$$E_{VDW} = D_0, ij \left[\left(\frac{R_{0,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{0,ij}}{r_{ij}} \right)^6 \right] \tag{3}$$

$$E_{bond\ strech} = K_1 (r_{ij} - r_0)^2 \tag{4}$$

$$E_{angle\ bend} = K_2 (\theta_{ijk} - \theta_0)^2 \tag{5}$$

The Lammps software conducted for the simulations is an atomic-molecule parallel simulator that efficiently calculates large-scale systems and thereby obtaining enough data to improve reliability [42].

The system time step is set as 1 fs and the temperature is set as 300 K. The specific simulation process is as follows: firstly, the ettringite substrate is "frozen" by a rigid body method, and only the water molecules and ions move and relax for 1000 ps under the NVT ensemble; secondly, the ettringite substrate was released and the whole system was operated for 500 ps to achieve thermodynamic equilibrium; finally, a 3000 ps balance was performed under the NVT ensemble. In this process, the velocity and trajectory information of all the atoms was recorded starting from the release of the substrate. The density distribution, radial distribution function, time correlation function and diffusion speed of water molecules or ions can be obtained by analyzing the extracted data. The mechanism of microscopic reaction is elucidated through exploring the interaction of ettringite with water and ions.

3. Results and discussion

3.1. The molecular structure of interfacial water molecules

3.1.1. Density distribution

The density profile well reflects the distribution of water molecules in the nanometer channel perpendicular to the substrate, which gives first insight on the spatial relationship between water molecules and ettringite interface. The water distribution is basically symmetrical, so half of the density profile is taken for analysis. As shown in Fig. 2b, it can be seen that there are three pronounced peaks in the region of the ettringite solid (z < 15 Å) for O$_w$ density profile at 2.5 Å, 8 Å and 13.5 Å, and five peaks with lower intensity at 0.5 Å, 4.5 Å, 6 Å, 9.8 Å and 11.2 Å. It indicates that a large amount of structural water molecules are orderly arranged in the ettringite substrate. Under geometric