

# Water and ions transport in calcium silicate hydrate: a molecular dynamics study

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## ABSTRACT

Transport properties of water and ions in calcium silicate hydrate (C-S-H) greatly affect the durability of cementitious materials. In this study, molecular dynamics (MD) technique is used to investigate the transport behaviors of NaCl solution in C-S-H nanopores with different sizes (from 0.5 nm to 5 nm), and the hindering effect of C-S-H on the diffusion of water molecules and Cl ions is further explored in the case of a 5 nm pore. Results show that the diffusion coefficients of water molecules and Cl ions in C-S-H nanopores increase with the expansion of nanopore. At the atomic scale, the Ca-rich C-S-H forms Ca-O and Ca-Cl clusters with water molecules and Cl ions, respectively, and the Si-O tetrahedra on silicate chains can also build hydrogen bonding interactions with water molecules, which constrain the transport behaviors of water and ions. From the molecular perspective, this study innovatively investigates the effect of C-S-H pore size on the diffusion capacity of water and ions, and reveals the chemical bonding mechanism between water molecules, Cl ions and C-S-H, which provides a theoretical basis for studying the resistance of concrete to ionic attack.

## 1. INTRODUCTION

Concrete structures serving in the marine environment, such as offshore structures and bridge piers, are susceptible to penetration by external water and harmful ions due to initial micro-cracks and pores [1,2]. The permeability of water and ions will inevitably affect the durability of concrete structures. For example, harmful ions (e.g. chloride ions) diffused into concrete materials may lead to internal steel corrosion and damage, thus reducing the service life of the overall structure [3,4]. Therefore, it is necessary to have a comprehensive understanding of the transport and permeability of water molecules and harmful ions in concrete materials.

Currently, lots of studies on the transport of water and ions in concrete are based on the experimental level. For example, many literatures elaborate and analyze the transport mechanisms of water and ions in concrete by many techniques including quasi-elastic neutron scattering [5], and <sup>35</sup>Cl NMR methods [6,7]. However, it is difficult to discover the micro mechanisms of water and ion transport in cementitious materials using only experimental studies. Fortunately, the rise of molecular dynamics (MD) simulation techniques offers the possibility to

clarify the intrinsic mechanisms of water and ion transport in cement materials.

Molecular-scale simulations allow visualization of water and ion transport processes in cementitious materials, and it can also provide some valuable information for developing concrete durability. These operations first require clarification of the transport properties of water and ions in various cement hydration products. As the most important substance in the cement hydration products, calcium silicate hydrate (C-S-H) is the direct source of concrete strength [8,9]. The transport of water and ions into C-S-H is an important factor affecting the durability of concrete materials [10]. Specifically, water is the carrier of harmful ions, and its presence is closely related to freeze-thaw, drying shrinkage, and creep of concrete [11]. At the same time, the chemical reaction of harmful ions with hydration products such as C-S-H may weaken the bond strength of cementitious materials and damage their microstructure. Therefore, it is of great significance to study the transport of water and ions in C-S-H from the molecular scale.

In this paper, the transport behaviors of NaCl solution in C-S-H and the diffusion patterns of water and ions in C-S-H nanopores of different sizes are investigated based on the MD technology.

Subsequently, the bonding interactions between water molecules, Cl ions and the C-S-H matrix are analyzed to further reveal the hindering effect of C-S-H on water and ion transport. The research results provide a theoretical basis for solving concrete durability problems.

## 2. SIMULATION METHOD

### 2.1 Model Information

The molecular models are constructed in the following steps. Firstly, a C-S-H gel model with Ca/Si ratio of 1.7 is constructed using tobermorite 11Å as the initial structure [12], as suggested by Pellenq et al. [13]. A part of the silica-oxygen tetrahedra located on the silicate chains are randomly removed, along

with the calcium ions located in the interlayer region, as shown in Figure 1(a). This operation allows the C-S-H gel model to match the experimentally obtained Q species distribution [14]. Subsequently, the C-S-H gel model is supercellularized and cleaved along the [0 0 1] direction to produce gaps with widths of 0.5, 1.1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 nm to simulate C-S-H nanopores. Then, a 0.4 mol/L NaCl solution with a density of 1.02 g/cm<sup>3</sup> is constructed, as depicted in Figure 1(b), which will be absorbed into the C-S-H nanopores with different sizes to investigate the transport behaviors of water and ions in the C-S-H nanopores. An example of the constructed molecular models is illustrated in Figure 1(c).

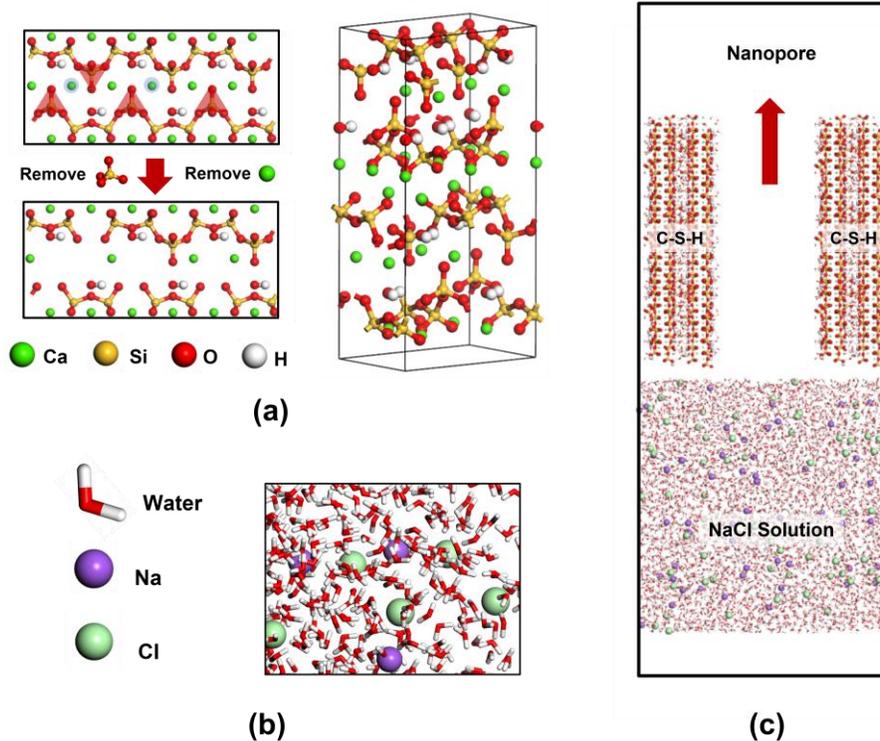


Figure 1. Molecular model of (a) C-S-H matrix, (b) NaCl solution and (c) transport nanopore model

### 2.2 Force Field

The interatomic interactions between NaCl solution and C-S-H matrix are computed by ClayFF force field [15,16], which has been widely used to simulate the adsorption and diffusion behaviors of water and ions in the layered structured phases. Previous works on various cement phases, such as tobermorite and portlandite, have confirmed the suitability of ClayFF for the simulation of calcium silicate systems [17,18].

### 2.3 Simulation Detail

All MD simulations are carried out on the LAMMPS platform [19]. In the NVT ensemble, the C-S-H matrix and the NaCl solution are relaxed for 1 ns at 298 K and 1 atm, respectively, to obtain a relatively reasonable molecular configuration. During this

period, the NaCl solution is kept isolated from the C-S-H matrix, i.e., there is no interactions between the two. Subsequently, the "Isolation" between the NaCl solution and the C-S-H matrix is removed, and a 2 ns MD simulation is performed at 298 K temperature under the NVT ensemble. In this 2 ns simulation, water and ions transport into the C-S-H nanopores. Meanwhile, atomic trajectories are recorded in real time for subsequent data analysis.

## 3. RESULT AND DISCUSSION

### 3.1 Size effects of C-S-H nanopores on water and ion diffusion

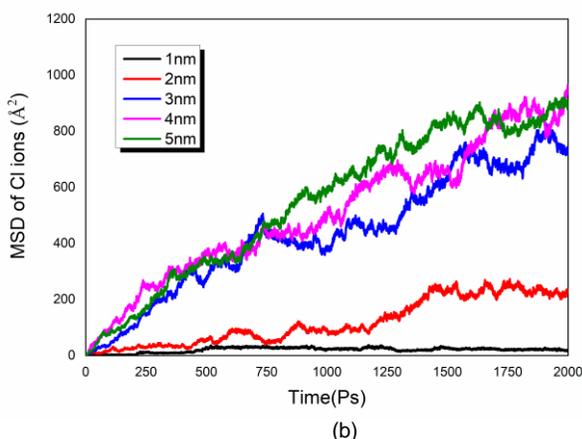
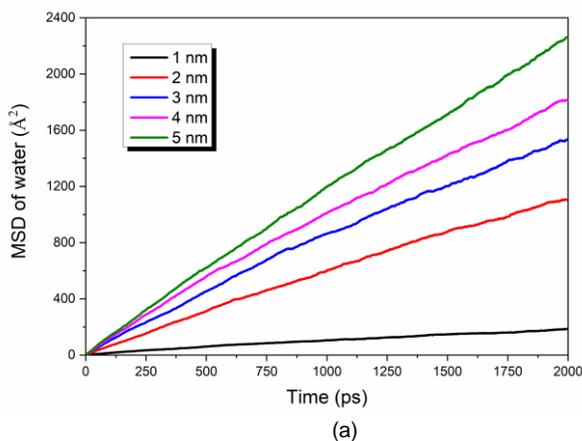
In this section, the diffusion capacity of water and ions transported in C-S-H nanopores with size from 0.5 nm to 5 nm are investigated.

Diffusion coefficient ( $D$ ) is usually used to evaluate the diffusion capacity of water and ions in C-S-H, which can be calculated indirectly by analyzing the mean square displacement (MSD) [20], as given in Equations 1 and 2.

$$MSD(t) = \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

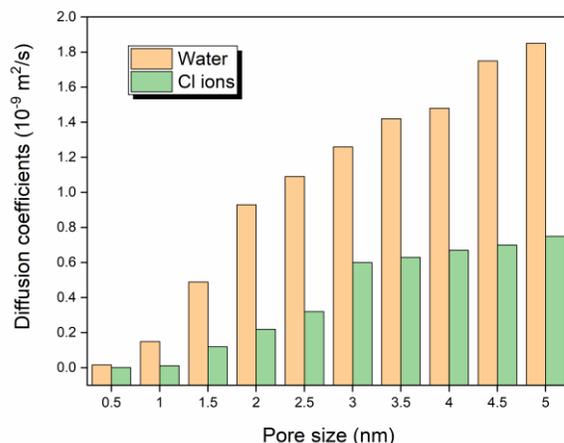
$$D = MSD / 6t \quad (2)$$

Figure 2 presents the MSD curves of water and Cl ions transported in the C-S-H nanopores with different sizes. It can be observed that the slope of the MSD curves for both water and Cl ions increases as the C-S-H nanopores become wider, which indicates that the diffusion of water and Cl ions is accelerated when the pore size increases. Besides, from Figure 2(a), the slope of the MSD curve for water molecules does not change with increasing simulation time, which indicates that the diffusion rate of water molecules does not change significantly throughout the MD simulation. In contrast, as shown in Figure 2(b), the MSD curve of Cl ions fluctuates and the slope changes significantly with time, which is mainly attributed to the fact that the number of Cl ions is much less than that of water molecules, affecting the calculation of the MSD average.



**Figure 2.** Mean square displacement of (a) water molecules and (b) Cl ions as a function of simulation time

Subsequently, the diffusion coefficients of water ( $D_w$ ) and Cl ions ( $D_{Cl}$ ) are calculated according to Equation 2, as listed in Figure 3. As the C-S-H nanopores become wider,  $D_w$  and  $D_{Cl}$  increase, which implies that the ability of the C-S-H matrix to inhibit the transport of water and Cl ions in the nanopore diminishes with increasing pore size. It is also found from Figure 3 that the  $D_w$  are always higher than  $D_{Cl}$  in C-S-H nanopores with the same size, indicating that the diffusion rate of water molecules is faster than that of Cl ions, which mainly stems from the fact that the C-S-H matrix has different influences on water and Cl ions, and this will be further discussed in Section 3.2. In addition, the calculated  $D_w$  and  $D_{Cl}$  in the 0.5 nm pore are extremely small, indicating that the water ultra-confined in the C-S-H matrix has a glassy nature [21].



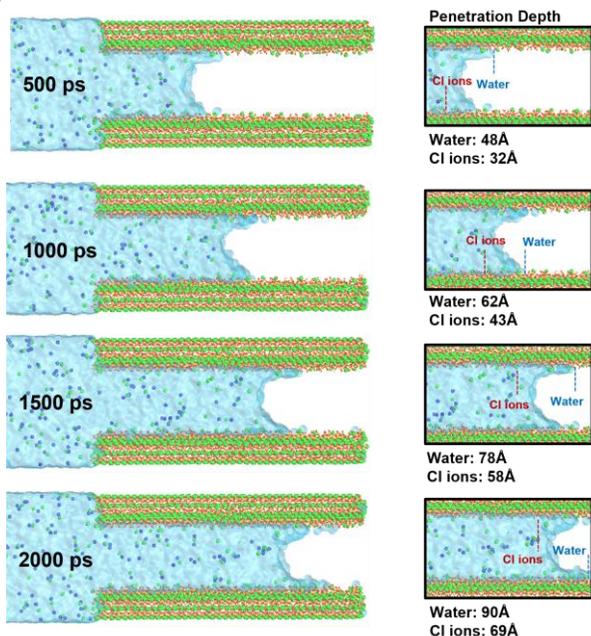
**Figure 3.** Diffusion coefficients of water and Cl ions in the C-S-H nanopores with different pore sizes

### 3.2 Interatomic hindrance mechanism of C-S-H on water and ion transport

In this section, the MD results of NaCl solution transport in C-S-H nanopores with the size of 5 nm are used to investigate the effect of C-S-H matrix on water and Cl ions diffusion properties from the molecular scale.

Figure 4 shows the molecular configuration of NaCl solution transported in C-S-H nanopores at different simulation time. During the simulation, water and ions gradually diffuse into the C-S-H with a concave shape of the liquid surface front, which is consistent with the capillary absorption property. Besides, from Figure 4, water molecules and Cl ions are transported in the C-S-H nanopore at different rates. The penetration depths of water molecules reached 48 Å, 62 Å, 78 Å, and 90 Å at 500 ps, 1000 ps, 1500 ps, and 2000 ps, respectively, which are much greater than that of Cl ions at the same time. It indicates that the transport behaviors of Cl ions in the C-S-H lags behind that of water molecules owing to the fact that water is a carrier of ionic motion, which also confirms the result that water molecules

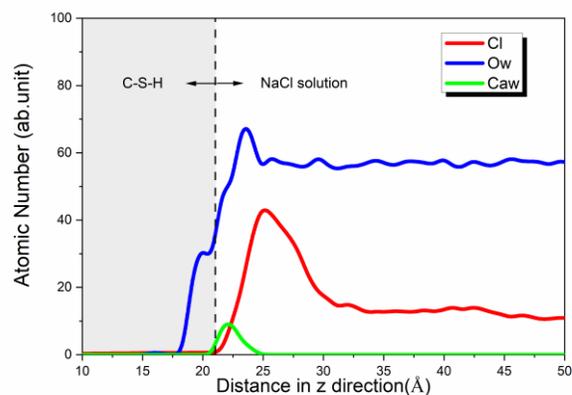
diffuse faster than Cl ions as described in the previous section.



**Figure 4.** molecular congruence and penetration depths of NaCl solution transported in C-S-H nanopores at different simulation time.

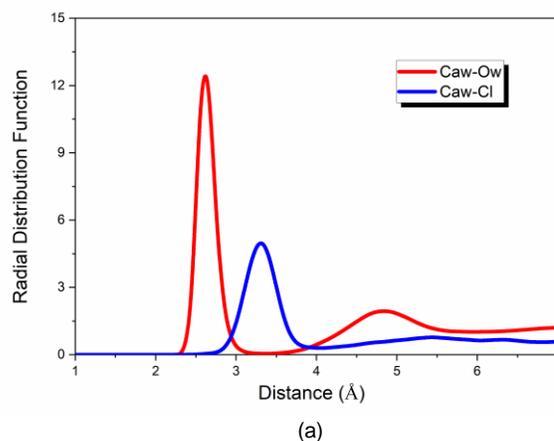
Transport result implies that the C-S-H matrix has a significant effect on the transport properties of water and Cl ions. Next, this effect of C-S-H on water and ion transport as described above will be further explored from the perspective of interatomic bonding interactions.

Figure 5 shows the atomic number curves of calcium ions (Caw), oxygen atoms of water molecules and Cl ions along the direction perpendicular to the C-S-H surface (Z-direction). The interface between the NaCl solution and the C-S-H matrix is located approximately at  $Z = 21.5 \text{ \AA}$ , as shown by the dashed line in Figure 5. Clear peaks can be observed in the atomic number curves of Ow and Cl at  $23.17 \text{ \AA}$  and  $24.76 \text{ \AA}$ , respectively, close to the peak position of the atomic number curves of Caw ( $22.36 \text{ \AA}$ ), implying the existence of relatively stable interactions (i.e., ion aggregation) between Caw and Ow and between Caw and Cl ions. However, when moving away from the C-S-H surface ( $Z > 35 \text{ \AA}$ ), the atomic numbers of Ow and Cl remain almost constant with increasing distance from the surface line, which means that the effect of the C-S-H matrix on water and ions almost disappears when moving away from the surface beyond  $10 \text{ \AA}$ . It is also observed from Figure 5 that the atomic number curve of Ow shows a peak on the left side of the surface line, which suggests that some of the water molecules cross the C-S-H surface and penetrate into the shallow region of the C-S-H matrix.

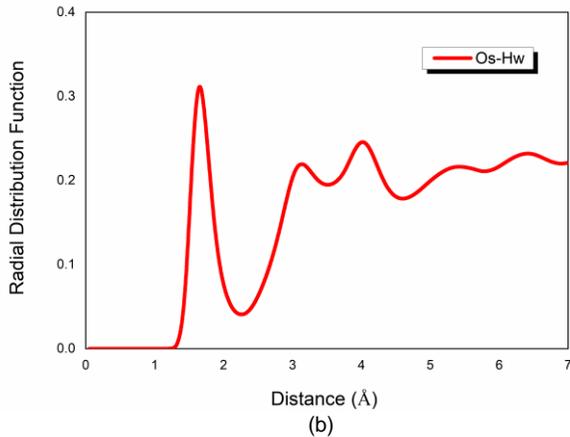


**Figure 5.** Atomic number curves of Caw, Cl ions and Ow atoms

Radial distribution function (RDF) is widely used to study the ordering and relative position relationship between two particles. In this study, the RDF relationships between water molecules, Cl ions and C-S-H surface particles are calculated to reveal the interactions of them. Figure 6 shows the RDF curves of Caw-Ow, Caw-Cl and Os-Hw, respectively, where Os denotes the oxygen atoms on the silicate chain of the C-S-H matrix and Hw denotes the hydrogen atoms in the water molecule. From Figure 6(a), the RDFs of Caw-Ow and Caw-Cl have peaks around  $2.65 \text{ \AA}$  and  $3.35 \text{ \AA}$ , respectively, which indicate a clear spatial correlation between Caw and Ow or Caw and Cl. It is mainly attributed to the attraction of positively charged Caw ions on the C-S-H surface to negatively charged particles in the NaCl solution. From Figure 6(b), the RDF curve of Os-Hw shows a peak at  $1.65 \text{ \AA}$ , indicating that Hw atoms can form hydrogen bonds with Os atoms.

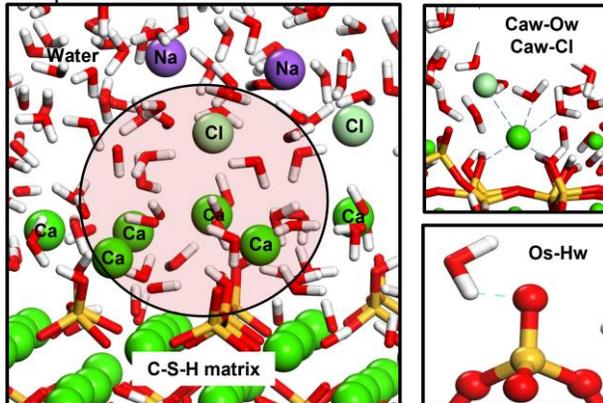


(a)



**Figure 6.** Radial distribution function of (a) Caw-Ow, Caw-Cl and (b) Os-Hw

The typical simulated snapshots of the interfacial region are depicted in Figure 7. It can be seen that the bonding structures are formed between water, ions, and C-S-H matrix, including Caw-Ow and Caw-Cl clusters, as well as the Os-Hw hydrogen bonds. Therefore, the ion clusters and the hydrogen bonding networks together form the interaction force between C-S-H and NaCl solution, which constrains the diffusion of water and ions and affects their transport in C-S-H.



**Figure 7.** Simulated snapshots of the interfacial region, and the bonding structures between water, ions, and C-S-H (Caw-Ow and Caw-Cl clusters and Os-Hw hydrogen bonds)

#### 4. CONCLUSIONS

When the size of C-S-H nanopore increases, the inhibitory effect of C-S-H on the transport of water and ions decreases and the diffusion rate of water and chloride ions accelerates.

In the C-S-H models (pore size from 0.5 nm to 5 nm), the diffusion coefficient of water molecules is always higher than that of chloride ions transported in the same size of C-S-H, indicating that the diffusion rate of water molecules is faster than that of chloride ions.

The effect of C-S-H on the transport of water and ions is significant. In the regions close to the C-S-H surface, the atomic number of water molecules and Cl ions is significantly higher than that inside the

NaCl solution. The Ca-rich C-S-H limits the diffusion of water molecules and Cl ions by forming Caw-Ow and Caw-Cl clusters. In addition, Si-O tetrahedra on silicate chains can also form hydrogen-bonding interactions with water molecules, thus impeding water and ion transport.

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