



Experimental and molecular dynamics studies on the transport and adsorption of chloride ions in the nano-pores of calcium silicate phase: The influence of calcium to silicate ratios



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ABSTRACT

Chloride transport in the gel pore determines the durability of concrete material. In this paper, experiments and molecular dynamics (MD) simulation were utilized to systematically investigate chemical composition (calcium to silicate ratio C/S) influence on the transport and adsorption behavior of water, calcium and chloride ions confined in the nano-pores of calcium silicate hydrate (C-S-H). The immersion experiments indicate C-S-H samples with higher C/S ratio have better chloride adsorption capability and the zeta potential measurements proved the calcium ions can determine the surface potential in the system and strongly affect the chloride adsorption. In the MD simulation, with increasing C/S ratio, the long surface silicate chains are broken to defective short chains that can provide more non-bridging oxygen sites to accumulate surface water molecules and calcium atoms. There existed strong spatial correlation between surface calcium and chloride ions in the radial distribution function patterns, which confirms that the surface calcium plays critical role in chloride adsorption. Furthermore, the interaction mechanism between calcium and chloride ions can be categorized into two parts, the stronger one caused by the formation of ionic pairs Ca-Cl (within 3 Å), and the weaker interaction at larger distance (around 4–6 Å). Therefore, high calcium concentration in the vicinity of surface contributes to stronger chloride adsorption, more Ca-Cl accumulation and longer resident time.

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1. Introduction

The properties of water molecules and ions ultra-confined in nanometer channel of porous materials have been widely investigated by researchers from various fields including the catalyst synthesis in the chemistry, the digestive process of animals in the biology, moisture transport in civil engineering materials and so on [1–3]. Due to the size effect of nano-pores and the strong influence of charged surface, these ultra-confined water molecules and ions behave extraordinary differently as compared with their bulk

counterpart. As the reference [4] in Nature mentioned, the first layer of water molecules can adsorb on the charged surface because of their polar nature and afterwards other layers can accumulate one by one, constituting a multilayered network of water molecules, which may have remarkably different physical properties as compared with standard liquid water. The layering and structuring of water molecules can increase the viscosity of the aqueous solution, leading to the drop of diffusion coefficients of ions in the solution [5].

Calcium silicate hydrate (C-S-H), one of the main hydration products of cement-based materials, has ill-crystallized structure with ubiquitous distributed gel pores with size ranging from 0.5 to 10 nm [6]. The transport and adsorption of water molecules in these gel pores can directly determine the chemical and physical properties of cementitious materials, strongly affecting the strength, creep, shrinkage and durability. On the other hand, the corrosion of

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reinforcing steels caused by chloride ions ingress is considered as the most serious durable problems in RC structures [7]. Therefore, it is of great importance to study the transport and adsorption of water molecules and chloride ions in the nano-pores of C-S-H gels.

The water in C-S-H gels has been categorized into three types by employing ^1H nuclear magnetic resonance (NMR), including chemical bound water that forms strong chemical bond with the cement hydrate, physical bound water deeply restricted near the surface and capillary water with little effect imposing from the cement hydrate [8–10]. The diffusion coefficients of different types of water molecules have been characterized by means of quasi-elastic neutron scattering (QENS) technique [11]. As for chloride ions, Ramachandran [12] claimed the chlorides in C-S-H could have three possible states of being chemisorbed, in the interlamination and in the lattice. Also using NMR, Yu and his coworkers [13] compared the relaxation time of chlorides located in jennite suspension and bulk aqueous solution respectively, and concluded the adsorbing chloride ions had similar chemical environment with the free ones and they exchanged rapidly, which indicated chloride ions were loosely bound on the surface of jennite. Furthermore, as the key parameter, the calcium to silicate ratio (C/S) was found to greatly affect the interaction between C-S-H and chloride ions [14,15]. It was observed in the scanning transmission X-ray microscopy with the resolution of 10 nm that high C/S C-S-H samples were able to bind more chlorides.

The numerical calculation method, molecular dynamics (MD), based on the force field, can help give a more quantitative understanding on the dynamics, energy and structure of water molecules and ions in the solid-liquid interfaces. Youssef et al. [16] concluded from the MD simulation that the C-S-H surface is hydrophilic due to the widely distributed non-bridging oxygen sites provided by the defective silicate chain. Manzano et al. [17] found that by applying a reactive force field in the simulation system, water dissociation and silicate polarization can occur in the solid-liquid interfaces and the surface Si-OH groups can be produced. Qomi's studied the influence of C/S ratios, and found that the chemo-physical properties of water molecules depended on the composition of surface [18]. These works mainly focused on the structural water molecules that exist in the interlayer region of calcium silicate hydrate. Kalinichev et al. developed the ClayFF force field and introduced it into the cement system. The structure, dynamics and energy of water and ions in the C-S-H gel pore were well simulated by ClayFF force field [19] and the water molecules confined in mineral nano-pores such as brucite layers were also investigated [20]. Employing this force field, Kalinichev et al. [21] and Hou et al. [22,23] also studied the transport and adsorption of chloride ions in nano-pores of main cement hydration product including C-S-H, ettringite, portlandite and C-S-H mineral analogues - tobermorite and jennite, respectively. They both concluded that few chloride ions could adsorb stably on C-S-H due to the negative-potential surface but their diffusion coefficients near the solid/liquid interface might be influenced. Simultaneously, in a clay-salt system MD simulations [5] showed that the salt diffusion coefficients strongly depended on the viscosity of water molecules. As stated above, the layering of water molecules increased the viscosity and thus contributed to a dramatic reduction of chloride diffusion coefficients. In our group's previous work, the low diffusion coefficients of chlorides in the

vicinity of C-S-H substrate can be attributed to the formation of Ca-Cl ion pairs that can strongly limit the movement of chlorides [24].

In this research, C-S-H samples were synthesized and the purity, composition and morphology were characterized systematically by X-ray diffraction (XRD), thermogravimetric analysis (TG) and scanning electron microscopy (SEM). Afterwards, on the one hand, immersion tests and zeta potential measurements were performed to show the macroscopic adsorption behavior of chlorides on synthesized C-S-H samples. On the other hand, the chloride adsorption mechanism was further investigated at atomic scale by the MD computation of the established sandwich-like models, in which the calcium chloride solution was confined in C-S-H interlayer pores. To quantitatively illustrate the interaction mechanism, several parameters were calculated including atomic density distribution normal to the substrate, atomic trajectories in the plane parallel to the substrate, radial distribution functions, coordination and H bond structure of ions, diffusion coefficients of ions and the interaction between ions. More importantly, the influence of C/S, which is the C-S-H properties-determining parameter, on chloride adsorption behaviors and mechanisms was the focus of this work, aiming at providing guidelines and support to the selection of cement and concrete materials exposed to chloride corrosion.

2. Experimental and computational method

2.1. Experimental method

2.1.1. Synthesis of C-S-H samples

C-S-H samples were synthesized at room temperature by mixing calcium oxide (CaO) and silica oxide (SiO_2) into the de-ionized water. CaO was obtained by calcining calcium carbonate above 1100 °C for over 3 h. SiO_2 was from Aero2000, Evonik with the nanoscale fineness to ensure high reactivity. The de-ionized water was boiled before the mix to remove solvated carbon oxide. To get C-S-H samples with the target C/S ratios, different molar ratios of CaO to SiO_2 were mixed according to Table 1, and the water to solid ratio is 10. The reaction duration was 3 weeks, after which the filtration and desiccation were performed. The solid and liquid phases were separated by a 0.45 μm nylon filter, and then dried until analysis in N_2 filled desiccators in the presence of saturated CaCl_2 solutions ($\approx 30\%$ RH) and NaOH pellets as CO_2 trap [25]. All operations were carried out in the glove box with the atmosphere of N_2 to minimize the CO_2 contamination.

2.1.2. Characterization of C-S-H samples

Several techniques including X-ray diffraction (XRD), thermogravimetric analysis (TG), scanning electron microscopy (SEM), and X-ray fluorescence (XRF) were employed for C-S-H samples characterization. XRD patterns were obtained by Bruker D8 Advance instrument of AXS, with Cu $K\alpha$ radiation at 15 kV, 50 mA. The scanning range was 5–80°(2 θ) with the speed being 0.02°/s. TG measurements were performed by SDT-Q600 Simultaneous Thermal Analyzer with around 10 mg sample heated in N_2 atmosphere and the increase rate of temperature was 10 °C/m. SEM images were taken by Quanta 250 Field Emission Scanning Electron Microscope produced by Company FEI with acceleration voltage being 20 kV. The ADVANT' XP Sequential XRF from Thermo Scientific was

Table 1
Composition of reactants and real C/S of the synthesis C-S-H samples.

Target C/S	Mass of CaO/g	Mass of SiO_2 /g	Mass of water/g	Real C/S measured by XRF
0.66	19.06	30.94	500	0.696
1	24.14	25.86	500	1.026
1.5	29.17	20.83	500	1.552

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