

# Diffusion study for chloride ions and water molecules in C-S-H gel in nano-scale using molecular dynamics: Case study of tobermorite

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**Abstract.** Porous materials such as concrete could be subjected to aggressive ions transport. Durability of cement paste is extremely depended on water and ions penetration into its interior sections. These ions transport could lead different damages depending on reactivity of ions, their concentrations and diffusion coefficients. In this paper, chloride diffusion process in cement hydrates is simulated at atomistic scale using molecular dynamics. Most important phase of cement hydrates is calcium silicate hydrate (C-S-H). Tobermorite, one of the most famous crystal analogues of C-S-H, is used as substrate in the simulation model. To conduct simulation, a nanopore is considered in the middle of simulation cell to place water molecules and aggressive ions. Different chloride salts are considered in models to find out which one is better for calculation of the transport properties. Diffusion coefficients of water molecules and chloride ions are calculated and validated with existing analytical and experimental works. There are relatively good agreements among simulation outputs and experimental results.

**Keywords:** molecular dynamics; C-S-H; cement; diffusion; durability; porosity; chloride ion; water molecule

## 1. Introduction

Cement is one of the most ubiquitous materials in the world. After water, concrete is the second most consumed substance on Earth. On average, three tons of concrete are consumed annually by every human living on the earth. Cement production industry accounts for around 5-7% of global carbon dioxide (CO<sub>2</sub>) emissions. Despite its other pollutions, this industry is in the third rank of producing greenhouse gases in the world. Moreover, cement production is the third most energy consumer industry (Hendriks *et al.* 1998). Based on these facts, there is a critical need to reduce cement consumption for saving our environment. Due to industrialized and modern life requirements and population increase, cement consumption is increasing in the world. There are several strategies to reduce cement consumption. Quality improvement of cement pastes and using cement alternative materials could be the most efficient ways to aim this purpose. In other words, to have longer lifetime for concrete structures, strength and durability of cement pastes must be

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one order of magnitude smaller than the chloride diffusivity in a pure salt solution system and diffusion coefficient of chloride ion in porous cement paste is  $1.07 \times 10^{-10} \text{ m}^2/\text{s}$  (Pivonka *et al.* 2004). This finding has chosen as basis for many other studies implemented by researchers recently (Zheng and Zhou 2008, Du *et al.* 2015).

Ingression rate of chloride ions into concrete is highly dependent on the internal pore structure (Yang *et al.* 2015). In cement paste, chloride ions transport through micropores (Buenfeld *et al.* 1998) and continuous pathways created by percolation of them (Garboczi and Bentz 1992). However, when the micropores close off, diffusive transport of ions would be carried out through nanopores (Garboczi and Bentz 1992, Zheng and Zhou 2008). Modelling of micropores through atomistic simulation of cement paste needs huge supercell size that could extremely increase computational costs. Therefore, diffusion properties of cement paste could be studied through nanopores at the molecular level. Many studies have been conducted to assess diffusion process by molecular simulations such as investigating adsorption and diffusion behaviors of ethanol/water through silicalite membrane (Yang *et al.* 2007), transport evaluation of chloride ions in hydrated cement paste subjected to NaCl solution (Pan and Liu 2009), studying binding capacity of C-S-H phases towards the migrating chloride ions at the water/solid interfaces (Pan *et al.* 2010) and assessment of water and ions transport in nanopores of tobermorite (Hou and Li 2014). Hou and Li (2014) analyzed atomic density and orientation profiles of calcium and water, H-bond network, diffusion coefficient of water and interactions between chloride ions and tobermorite.

In this paper, diffusion of chloride ions and water molecules in pores of cement hydrates was investigated. Due to structural similarity, 11 Å tobermorite (Hamid 1981), was used to study transport properties of C-S-H gel at the nanoscale. Molecular dynamics (MD) was implemented to simulate diffusion in pores surrounded by cementitious hydrates. Simulation supercell size might effect on the analysis convergence. Optimum size of supercell was found to have lower computational costs and more exact results. Diffusion coefficient of chloride ions and water molecules was calculated using mean-squared displacement (MSD) approach. Moreover, density profile of water molecules was obtained.

## **2. Computational procedure**

### *2.1 Simulation model*

C-S-H gel is usually modelled by means of crystal mineral analogues. Hamid's 11Å tobermorite structure (Hamid 1981) is considered in this study. To have a crystal structure similar to real structure of C-S-H gel some modifications must be done such as adding calcium ions and hydroxyl groups to tobermorite structure (Kurczyk and Schwiete 1962), inclusion of tobermorite between portlandite sheets (Kantro *et al.* 1962), incorporation of silicate monomer groups in portlandite structure (Shpynova *et al.* 1967), considering some calcium ions and hydroxyl groups in the structure and interlayer spaces between silicate chains of tobermorite (Taylor and Howison 1956) and removing some bridging silicon tetrahedral groups and adding interlaminar calcium ions (Richardson and Groves 1992). In this paper, no modification has been considered in simulation model and original forms of above-mentioned crystals are studied.

For evaluating dynamic properties such as surface interactions and transportation characteristics, it is common to model substrates at the ends of simulation box and a nanopore in the middle of super cell which includes aqueous solution of anions and cations. This procedure has



Molecular dynamics (MD) is usually used to have a better insight about chemical and physical interactions between atoms or molecules and to calculate main properties of materials in the atomistic level (Gopalakrishnan *et al.* 2011). MD is suitable to calculate the time-dependent properties such as diffusion coefficient. In this research Molecular Dynamics method was conducted using Materials Studio software (Accelrys 2010). The temperature of simulation model was 27°C (300 K). System must be equilibrated before main Molecular Dynamics simulation. Therefore, MD simulations were implemented using 2000 ps running after total 300 ps relaxation stages for the system. NVT canonical ensembles were considered for the models, which the number of atoms or molecules in mole (N), volume (V) and temperature (T) of supercell were conserved and a thermostat exchanged the energy of exothermic and endothermic processes. Time step was set to 1 fs and frames were extracted every 100 fs, so that 20,000 different atomic configurations were stored to be analyzed later as trajectories. It must be mentioned that total time of simulation was greater than 0.5 ns, so that it was enough to guarantee statistical reliability. Moreover number of ions (more than 10) and dimensions of supercell was large enough to provide reliable results (Hou and Li 2014).

It is very important to describe forces and potentials between atoms of a molecule or a group of molecules with a set of functions and parameters in molecular dynamics. This is provided by force fields. In this study, Condensed-phase Optimized Molecular Potentials for Atomic Simulation Studies (COMPASS) (Sun 1998) was adopted that is an ab-initio force field that is a new version of PCFF force field. COMPASS force field could support energies of bond, angle, torsion, out-of-plane internal coordinates, cross-coupled internal coordinates, non-bond interactions, Coulomb potential and Lenard-Johns 9-6 potential (Sun 1998). Due to its mentioned capabilities and supporting potentials of interactions between different atoms and molecules in aluminosilicate materials, it is a proper to use in simulation of cement hydrates (Al-Ostaz *et al.* 2010).

### *2.3 Data analysis procedure*

Dynamic properties of water molecules and ions such as diffusion coefficients can be found from dynamics and kinetics studies. There are three common procedures to obtain diffusion coefficient. The first method uses velocity values of molecules (or ions). In this method diffusion coefficient would be calculated through integrating Velocity Autocorrelation Functions (VAF) such as Green-Kubo relations (Haile 1992). The second method is Force Autocorrelation Method which could be used to study diffusion over free energy barriers based on fluctuation-dissipation theorem (Marrink and Berendsen 1994). In this method, molecule at the position of interest will be fixed and the force acting on it in time,  $F(t)$  will be recorded. Time correlation of this force yields diffusivity. The third method uses molecule positions to calculate Mean Squared Displacement (MSD) for estimating diffusion coefficient. Results obtained in all methods are theoretically the same and proper method must be chosen depending on study goals. In this paper, Mean Squared Displacement method is preferred due to convenience of its calculation procedure, less computational costs and rare numerical problems.

Mean squared displacement could be computed using Eq. (1) and diffusion coefficient would be calculated through Einstein formula (Eq. (2)). Einstein found the relation between MSD and diffusion coefficient (Einstein 1956)

$$MSD = \frac{1}{N} \sum_{i=1}^N (\vec{r}_i(t) - \vec{r}_i(t_0))^2 = \langle [\vec{r}_i(t) - \vec{r}_i(t_0)]^2 \rangle = \langle \Delta \vec{r}(t)^2 \rangle \quad (1)$$



Table 1 Diffusion coefficients of chloride ions in cement

	Case	NaCl solution	CaCl <sub>2</sub> solution	KCl solution
MD simulation	tobermorite 11Å (present study)	$6.643 \times 10^{-10}$	$7.551 \times 10^{-10}$	-----
	tobermorite 11Å (Hou and Li 2014)	-----	$1.73 \times 10^{-9}$	-----
	tobermorite (Pan <i>et al.</i> 2010)	$2.334 \times 10^{-9}$	-----	-----
	portlandite (Pan <i>et al.</i> 2010)	$2.269 \times 10^{-9}$	-----	-----
	jennite (Pan <i>et al.</i> 2010)	$2.367 \times 10^{-9}$	-----	-----
	tobermorite 9Å (Kalinichev <i>et al.</i> 2007)	-----	-----	$3.8 \times 10^{-10}$
	cement paste (experimental) (Pivonka <i>et al.</i> 2004)		$1.07 \times 10^{-10}$	-----

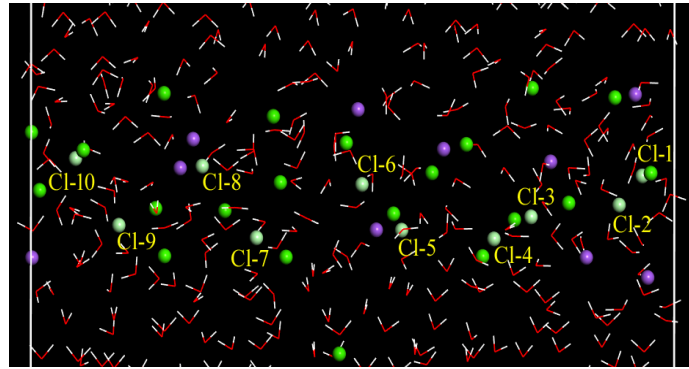


Fig. 3 Middle part of supercell that is enlarged to show labels of chloride atoms in NaCl solution. water molecules in white/red lines (hydrogen in white and oxygen in red), chloride atoms in cyan balls, sodium atoms in purple balls and calcium atoms in green balls

As described above, NaCl and CaCl<sub>2</sub> solutions were simulated separately. In Fig. 1 initial location of chloride ions are shown in the middle of length of specimen that they are away enough from tobermorite surfaces. Diffusion coefficient of ions near to surfaces could not be calculated correctly, but for away ions from substrates ( $>10 \text{ \AA}$ ) it could be achieved properly (Pan *et al.* 2010). Ions must be positioned at distance greater than 8-10 Å which is three-times the molecular diameter of water molecule (Kalinichev *et al.* 2007). Various ions and molecules were dislocated during MD analysis process. They have different locations in different output frames. Displacement path of chloride ions were traced and drawn in Fig. 2.

These trajectories show how different chloride atoms were moved during simulation time. Extracted trajectories indicate correctly that these solute ions were moved according to Brownian motion algorithm. Diffusion coefficients of different chloride ions are provided in Table 1. Chloride ion numbers are illustrated in Fig. 3.

It could be found that there are no large differences between diffusion coefficient of chloride ions in NaCl solution and of CaCl<sub>2</sub> solution. Total average of diffusion coefficient of chloride ions was obtained  $7.097 \times 10^{-10} \text{ m}^2/\text{s}$  that is closer to experimental results in comparison to previous simulation researches in the literature. It is found that an optimized value of chloride diffusion coefficient in cement paste is  $1.07 \times 10^{-10} \text{ m}^2/\text{s}$  which has obtained by comparing with a large number of experimental results collected from the literature (Pivonka *et al.* 2004).

In this study, no adsorption of chloride ions were observed by tobermorite surfaces. It is due to





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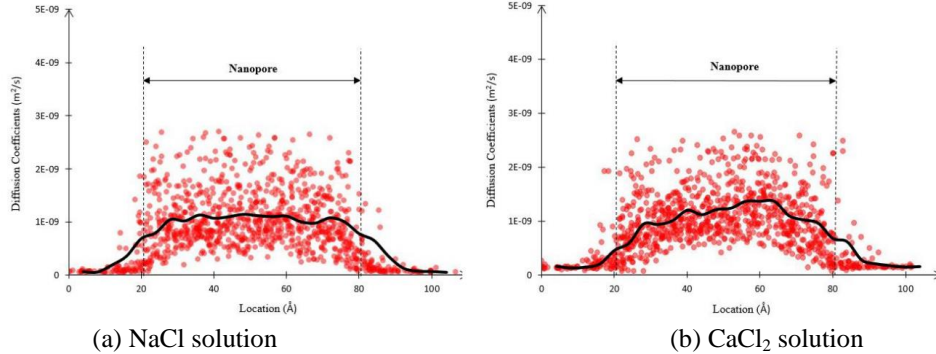


Fig. 6 Diffusion coefficients variation for water molecules with location in tobermorite model

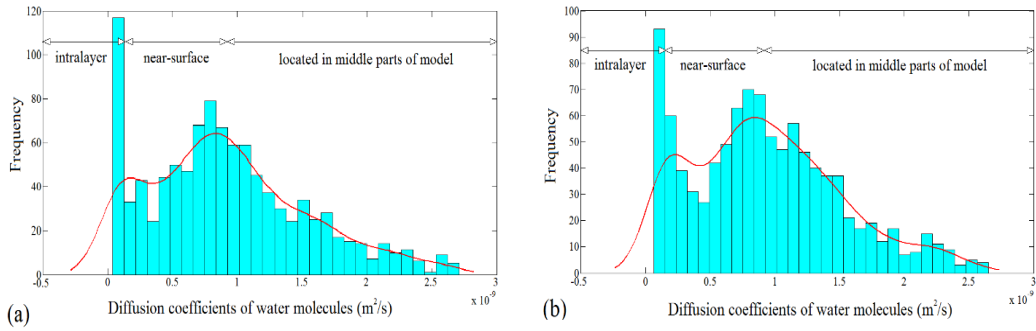


Fig. 7 Histogram of diffusion coefficients for water molecules in (a) NaCl model, (b) CaCl<sub>2</sub> model

of interactions between atoms. Final configuration of model yields density profile that is shown in Fig. 5. In this figure, densities of oxygen atoms of water molecules (OH<sub>2</sub>O) are drawn. As it could be found in this figure, local atomic densities of water molecules are highly different from centerline of model to the substrates. Peak of the profile shows that water molecules were concentrated near to substrates. Fig. 5 demonstrates that density of water molecules would be tended to 1 gr/cm<sup>3</sup> in middle parts. Therefore in the middle one-third of nanopore, density of water molecules remained unchanged and it was approximately near to its initial value. Fig. 5 also indicates that density profile of water molecules is symmetric relative to centerline of super cell.

Diffusion coefficients of all of the water molecules were calculated in simulated models. Fig. 6 shows diffusion coefficients variation of water molecules versus their initial locations in primary configuration. Diffusion coefficient of intra-layer water molecules are located at initial and end-part of diagram shown in Fig. 6. In this figure, curved line was drawn by computing average value of diffusion coefficients for specific locations. Water molecules in super cell could be categorized into two groups: intra-layer water molecules (molecules positioned between silicate chains which are part of tobermorite structure) and interlayer water molecules (molecules positioned in nanopore). The group of interlayer water molecules could be divided into two parts itself: near-surface water molecules and water molecules in middle one-third of nanopore.

In this paper, diffusion coefficient of intra-layer water molecules has been obtained about  $6.8 \times 10^{-11}$  m<sup>2</sup>/s that there is relatively good agreement with diffusion coefficient found previously by other researchers using MD simulation for water molecules located between silicate layers



molecules. Right side of the second peak is almost related to water molecules with the most distance to tobermorite surfaces and they had the greatest diffusion coefficients in super cell.

#### **4. Conclusions**

In this paper diffusion process in C-S-H, the most important phase of cement paste was assessed at nano scale using Molecular Dynamics (MD). Tobermorite 11Å was used as crystal mineral analogues to C-S-H. For this purpose, water molecules and chloride ions were placed in a nanopore which was considered at the middle of simulation cell. Different chloride salts including sodium chloride and calcium chloride were considered as solute salts in water. Using Einstein formula that is based on the mean squared displacement (MSD) method, diffusion coefficients of chloride ions and water molecules were obtained and validated with previous simulation researches and experimental works. In present study, diffusion coefficients of chloride ions in NaCl and CaCl<sub>2</sub> solutions have been obtained close to each other. Total average of diffusion coefficient of chloride ions was calculated as  $7.097 \times 10^{-10}$  m<sup>2</sup>/s. This value has better agreement with experimental results in comparison to previous MD simulation works in the literature.

Moreover, water diffusion coefficients in different locations of model have been computed. Confined water molecules between layers of tobermorite had very low diffusion coefficient. Large numbers of water molecules were adsorbed near to substrates and they had relatively low diffusivity because of significant influence of tobermorite surface to water molecules. Water molecules concentration in the near-surface domains was larger than other locations. In this domain, solid surface applied the adsorption forces and water molecules were relatively stabilized. Value of diffusion coefficient of water molecules in near-surface domains were comparable with experimental results from the literature obtained by PFCR and QENS methods. Diffusion coefficients of water molecules in the centerline of model were relatively tend to bulk water diffusion coefficient and they had greater values in comparison to other locations. The farther water molecules from tobermorite phases, the more analogue of their diffusivity to bulk water diffusion.

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