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_2) 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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increased.

It is shown that source of concrete strength and durability lies in the configuration of its nanoparticles. When the cement hydration initiates, chemical reactions lead to form the elementary building block of cement hydrates, mainly calcium-silicate-hydrate (C-S-H). MIT researchers discovered that C-S-H behavior always shows a unique nanosignature for different cement paste compositions, which they call the material's genomic code (Brehm 2007). C-S-H is the dominant phase occupying almost 60-70 percent of hydration products of cement-based materials. It is the most important phase of cement hydrated products that is mainly responsible for mechanical properties of cementitious materials. Its nanostructure is not completely understood. The atomic structure of C-S-H can be qualified as being intermediate, definitely not completely crystalline but not fully amorphous (Bauchy *et al.* 2014). Recently, advanced computers and novel techniques of simulation as well as modern experimental studies provided better insight for atomistic structure of C-S-H. Implementation of atomistic simulations for cementitious materials is relatively a new field. It is worth noting that molecular modelling studies recently have focused primarily on the structural properties of the cement hydrates (Tarighat *et al.* 2016). Because of complex structure of C-S-H, usually some crystalline silicate hydrates with similar structure would be used in the simulations such as tobermorite (Hamid 1981, Merlino *et al.* 1999), jennite and portlandite. Mechanical properties as well as durability-related parameters could be determined using first principle methods, molecular dynamics (MD) and Monte Carlo method (MC). Calculation of mechanical properties of C-S-H using MD is one of the research areas of interest for researchers. They found mechanical properties of C-S-H by simulating different supercell sizes (Al-Ostaz *et al.* 2010), force fields (Al-Ostaz *et al.* 2010, Tavakoli and Tarighat 2016), various C-S-H crystal mineral analogues (Hajilar and Shafei 2015) and Portland cement clinker phases (Tavakoli and Tarighat 2016). Mechanical properties of the cementitious C-S-H gel such as bulk (K), shear (G) and Young's modulus (E) in different Ca/Si and Ca/water ratios could be analyzed by force field calculations (Manzano *et al.* 2007, Hou *et al.* 2014) and its compressive and tensile strengths might be derived by using molecular dynamics (Murray *et al.* 2010). Moreover, cement hydrate properties have been optimized by simulating C-S-H as main binding phase of cement paste against different values of some structural parameters such as Calcium-to-Silicon ratio (Qomi *et al.* 2014).

Durability-related researches on atomistic scale of cement paste are most recent studies on simulation of cementitious materials. Concrete deterioration could be occurred due to physical or chemical factors. Chemical factors are categorized into internal and external causes. Deterioration caused by aggressive ions from surrounding environment is occurred mainly due to concrete excessive permeability. Studying diffusion of chloride ions is very important; because chloride ions could initiate corrosion of steel bars that are embedded in concrete structures. Content of chloride ions at various depths of concrete is stochastic (Tarighat 2012). Load bearing capacity of reinforced concrete elements could be strongly decreased (Tarighat and Zehtab 2016), if chloride ions concentration in concrete leads to steel corrosion. Many researchers studied diffusion process of chloride ions in porous materials such as concrete experimentally and theoretically. Diffusion process has long-term effects so that experiments conducted to assess this phenomenon take long time. It is possible to conduct diffusion experiment more rapidly by means of accelerated methods. Some of the experimental methods are based on electrochemical measurements such as rapid chloride penetration test (RCPT) (ASTM 2006, Miyandehi *et al.* 2014), accelerated chloride migration test (ACMT) (Yang and Cho 2003), short-term immersion test (Park *et al.* 2014), diffusion cell test (Pivonka *et al.* 2004) and transient techniques, etc. Chloride diffusivity is found

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 1.07×10^{-10} m^2/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
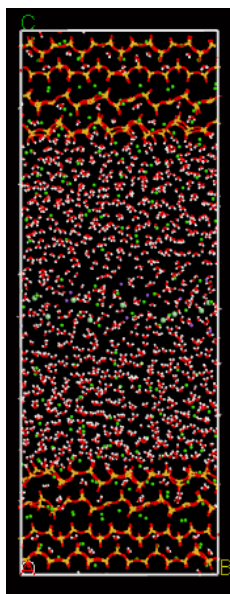
Fig. 1 Simulation model and confined water with ions in nanopore between tobermorite substrates. Silicate chains are in red/yellow lines (silicon in yellow and oxygen in red), water molecules in white/red lines (hydrogen in white and oxygen in red), chlorine atoms in cyan balls, sodium atoms in purple balls and calcium atoms in green balls

been implemented by previous researchers for tobermorite (Kalinichev and Kirkpatrick 2002, Hou and Li 2014) and other hydrates such as portlandite, Friedel's salt, AFm phases, Aft phases, brucite and gibsite (Kalinichev and Kirkpatrick 2002, Kirkpatrick *et al.* 2005, Kalinichev *et al.* 2007). Simulated supercell contains $2\times5\times1$ crystallographic unit cells. These replicated unit cells were located at top and bottom of super cell. Moreover a nanopore must be included in supercell to add aggressive solution. Gel pore sizes vary from 0.5 nm to 10 nm in hydrated cement paste (Mindess *et al.* 2003). It is illustrated that chloride diffusion could be accomplished through gel pore sizes smaller than 10 nm (Pivonka *et al.* 2004). Therefore width of nanopore must be selected in this range. In this study a pore of width 60Å was modelled between tobermorite substrates that it was filled with NaCl or $CaCl_2$ solution. Simulation model was illustrated in Fig. 1. It shows overall illustration of one of the simulated supercells which contains NaCl solution.

  Lattice parameters of simulated supercell are a=13.38 Å, b=36.95 Å, c=100.94 Å and α=90°, β=90°, γ=90°. Appropriate number of water molecules in the gel pore must be selected. Here 992 water molecules were added the pore volume of computational model so that density of bulk aqueous solution was about 1 g/cm^3 satisfying ambient conditions (Kalinichev and Kirkpatrick 2002). Corrosion could be initiated in different chloride ion concentrations depending on various environmental conditions and concrete mixtures (Moreno *et al.* 2004). In this paper a 0.56 M solution was used so that 10 chloride ions must be added to computational supercell. For NaCl and $CaCl_2$ solutions, 10 sodium atoms and 5 calcium atoms were used respectively to form corresponding salts. Moreover, 10 extra calcium atoms were added to compensate negative charge in the both systems.

2.2 Molecular dynamics

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)

$$MSD = \frac{1}{N}\sum_{i=1}^{N}\left(\vec{r}_i(t) - \vec{r}_i(t_0)\right)^2 = \left\langle \left[\vec{r}_i(t) - \vec{r}_i(t_0)\right]^2 \right\rangle = \left\langle \Delta\vec{r}(t)^2 \right\rangle \qquad (1)$$
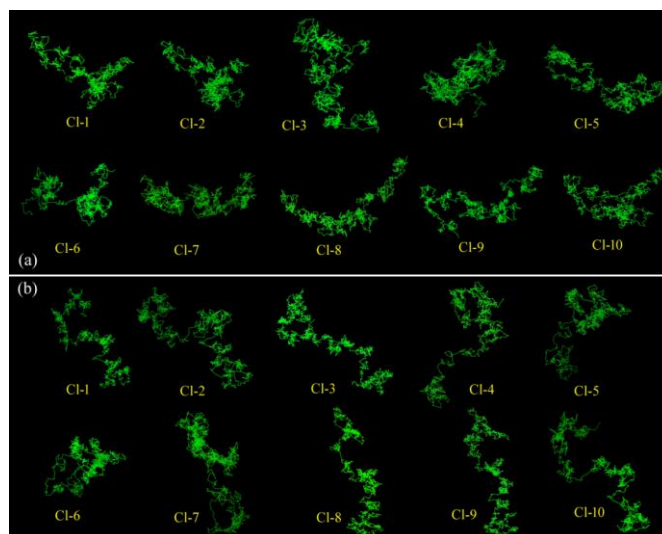
Fig. 2 Trajectories of chloride ions during simulation in (a) NaCl solution, (b) CaCl$_2$ solution

$$D = \frac{1}{2d} \lim_{t \to \infty} \frac{\left\langle \left[\vec{r}_i(t) - \vec{r}_i(t_0) \right]^2 \right\rangle}{t} = \frac{MSD}{2dt} \tag{2}$$

Where r_i is the location of ion (or molecule) at step i and N is the total number of frame extracted from simulation. D, t_0 and d are diffusion coefficient, initial time of simulation and dimensionality of the system (d=3 for three-dimensional system), respectively.

Well-known Einstein formula can be used to estimate diffusion coefficient when the calculation is converged. When the diagram of log (MSD) versus log (t) was linear, diffusive regime of system would be normal and MSD method is valid to estimate diffusion coefficient (El Amrani and Kolb 1993, Yang *et al.* 2007). MSD calculation must be stopped at step N/2 because the elapsed time is half the total time and all the MSD have the same number of data points contributing to them, and thus they are weighted equally (Keffer 2001). Second half of MSD data must be ignored, because they are not valuable due to very little data in computation of MSD at this part. Therefore, diffusion coefficient could be estimated by fitting a line in first half MSD diagram versus time. The slope of this line would be approximately equal to 6D for a 3-dimensional system and diffusion coefficient could be calculated as below

$$MSD=6Dt+fluctuations \tag{3}$$

Fluctuations term in Eq. (3) is written to emphasize that there are differences between approximated trend line and main curve. It is obvious that smoother fluctuation yields better approximation and higher R-squared value in regression. Using this method, diffusion coefficient of chloride ions and all of the water molecules in supercell were calculated and analyzed.

3. Results and discussion

3.1 Diffusion coefficient of chloride ions

Table 1 Diffusion coefficients of chloride ions in cement

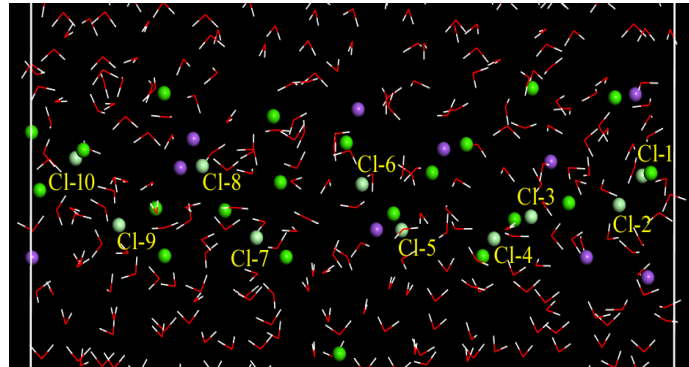|	Case	NaCl solution	CaCl$_2$ solution	KCl solution
	tobermorite 11Å (present study)	6.643×10^{-10}	7.551×10^{-10}	------
MD simulation	tobermorite 11Å (Hou and Li 2014)	------	1.73×10^{-9}	------
	tobermorite (Pan *et al.* 2010)	2.334×10^{-9}	------	------
	portlandite (Pan *et al.* 2010)	2.269×10^{-9}	------	------
	jennite (Pan *et al.* 2010)	2.367×10^{-9}	------	------
	tobermorite 9Å (Kalinichev *et al.* 2007)	------	------	3.8×10^{-10}
	cement paste (experimental) (Pivonka *et al.* 2004)	1.07×10^{-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$_2$ 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 Å) 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$_2$ solution. Total average of diffusion coefficient of chloride ions was obtained 7.097×10^{-10} m^2/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 1.07×10^{-10} m^2/s which has obtained by comparing with a large number of experimental results collected from the literature (Pivonka *et al.* 2004).

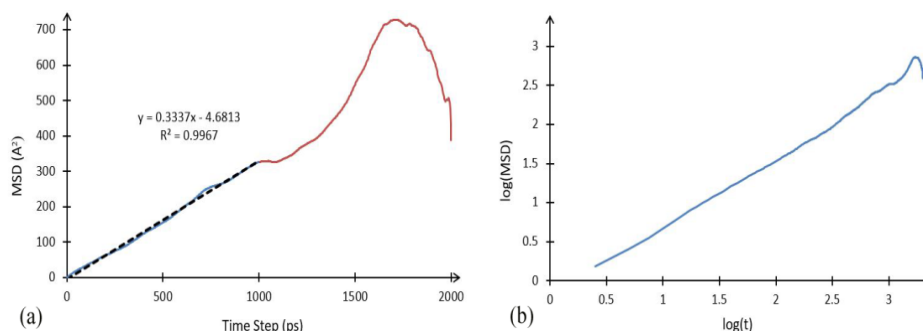In this study, no adsorption of chloride ions were observed by tobermorite surfaces. It is due to

Fig. 4 MSD values versus time for trajectory of chloride ion 1 (for example) in NaCl solution provided in the case of (a) linear-scale graph (b) logarithmic-scale graph
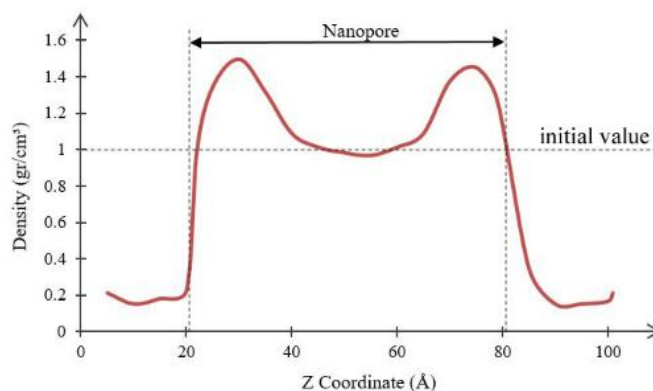

Fig. 5 Density profile of OH_2O in tobermorite model

low chloride ion binding capacity of tobermorite. This result is in good agreement with findings of previously-published researches. They reported that C-S-H phase such as tobermorite and jennite have low chloride sorption capacity (Kirkpatrick *et al.* 2001, Yu and Kirkpatrick 2001, Kalinichev and Kirkpatrick 2002, Pan *et al.* 2010).

Diffusion coefficient values were calculated using Einstein formula. Diffusion coefficients for each of the chloride ions were estimated by fitting a line on the diagram of MSD versus time. In Fig. 4(a), one of the diagrams which were implemented to calculate diffusion coefficient, is shown for instance. In this figure a line was fitted on the diagram from 0 to 1000 ps. Second half of diagram was ignored because of numerical problems that are discussed in section 2.3. Using slope of diagram, diffusion coefficient of chloride ion No.1 was obtained 5.562×10^{-10} m^2/s. Moreover log-log diagram of MSD versus time is drawn in Fig. 4(b). This diagram is linear and it shows that simulation was converged. Thus using Einstein formula to evaluate diffusion coefficient would be a reliable method.

3.2 Diffusion coefficient of water molecules

In the simulated model, there were 992 interlayer water molecules and 40 intra-layer water molecules for each substrate. Interlayer molecules were placed in nanopore channel and intra-layer water molecules were parts of tobermorite structure. These molecules might be dislocated because

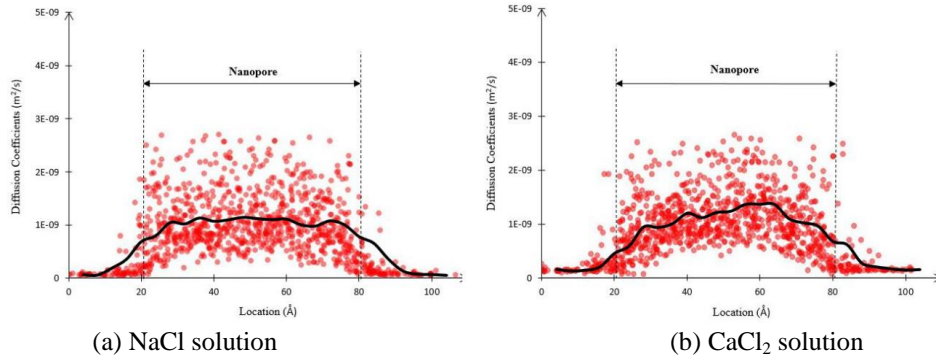(a) NaCl solution   (b) CaCl$_2$ solution

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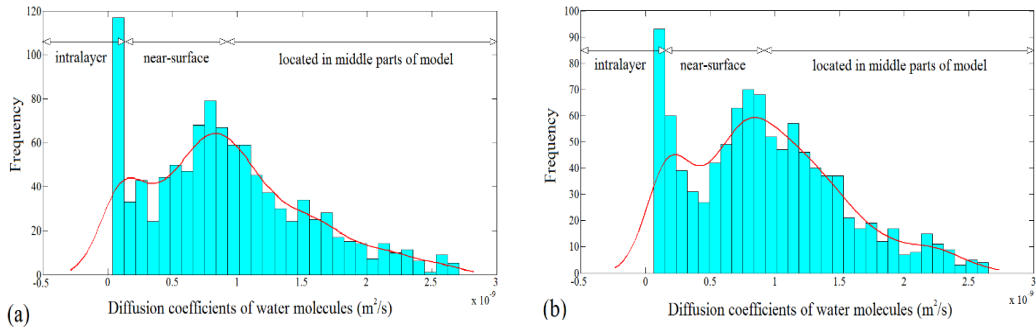

Fig. 7 Histogram of diffusion coefficients for water molecules in (a) NaCl model, (b) CaCl$_2$ model

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$_2$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^3 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 6.8×10^{-11} m^2/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

inside the tobermorite structure as 5.0×10^{-11} m^2/s (Kalinichev *et al.* 2007) and 1.4×10^{-11} m^2/s (Yoon and Monteiro 2013). As it was expected, diffusion coefficients of intra-layer water molecules were very small because of their glassy nature. They could oscillate around their initial locations with slow rate, since they were entrapped between silicate chains in the tobermorite structure and they have strong H-bonds.

Diffusion coefficients of water molecules located near to substrates were obtained about 4.5×10^{-10} m^2/s to 7.7×10^{-10} m^2/s in this study. These values are comparable with results that were previously obtained from PFCR (Korb *et al.* 2007) and QENS (Fratini *et al.* 2013). Diffusion coefficient of water molecules located between the C-S-H particles are reported in the literature that were experimentally found by a proton field cycling relaxometry approach (PFCR) $D = 0.68 \times 10^{-10}$ m^2/s (Korb *et al.* 2007) and Time-Resolved Incoherent Elastic Neutron Scattering (QENS) $D = 6.8 \times 10^{-10}$ m^2/s (Fratini *et al.* 2013). PFCR and QENS are two methods which are developed to find the dynamic properties of water molecules adsorbed in the nanopore surfaces (Hou and Li 2014). Water molecules near to surface of tobermorite were affected by interaction with silicate hydrates and they diffuse with lower rate comparing to molecules located at greater distance from substrates.

Diffusion coefficient of water molecules in middle parts of model has been calculated about 1.14×10^{-9} m^2/s and 1.23×10^{-9} m^2/s in NaCl and $CaCl_2$ models, respectively. Previous researchers have studied on bulk water diffusion coefficient and they found it 4.13×10^{-9} m^2/s that was obtained by SPC model (Hou and Li 2014). This conclusion can be drawn that water molecules in middle parts of super cell are less affected by tobermorite surfaces. Diffusion coefficients of these water molecules are greater than molecules located near to surfaces of tobermorite. So they can diffuse more freely in comparison with other water molecules in simulated super cell. The more distance away from tobermorite substrates, the more similarity of water molecules behavior to bulk waters.

In Fig. 7, histogram of diffusion coefficients of all of the water molecules are shown. Diffusion coefficients of water molecules shows a bimodal distribution. Mean value of diffusion coefficients of all water molecules were calculated as 0.92×10^{-9} m^2/s and 0.94×10^{-9} m^2/s for NaCl and $CaCl_2$ models, respectively and standard deviation value was obtained 0.61×10^{-9} m^2/s in NaCl model while it was 0.58×10^{-9} m^2/s for $CaCl_2$ model. In Fig. 7 the regions of three different types of water molecules have been drawn approximately. Diffusion coefficient values were greater for farther water molecules (see Fig. 6). Therefore it could be rational to assign greater values of histogram to water molecules positioned in intermediate parts of super cell and lower values to intra-layer water molecules. As it is illustrated in Fig. 6, diffusion coefficient values were dispersed and the region of each category of water molecules could not be showed exactly in Fig. 7. Moreover, molecules might be moved from one category to another through simulation time. However data provided in Fig. 7 have been analyzed qualitatively. Boundaries between three different regions are estimated based on number of water molecules corresponding to each range of diffusion coefficient values in each bar of histogram for each of the three different location group (location before MD simulation). This histogram has two peaks that first peak is accordingly corresponding to water molecules with low diffusivity that they are almost intra-layer water molecules and some of the near-surface water molecules which may tightly adsorbed. Diffusion coefficients of these water molecules at both ends of model were similar and their diffusion coefficient values created one peak in histogram, because of symmetry nature of super cell and density profile consequently. By matching the density profile and diffusion coefficient histogram, it could be found that large number of water molecules are adsorbed near to substrates which they have relatively low diffusivity. Most of the values according to second peak of histogram belong to near-surface water

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 $CaCl_2$ solutions have been obtained close to each other. Total average of diffusion coefficient of chloride ions was calculated as 7.097×10^{-10} m^2/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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