





Research Article

Diffusion study of chloride and binding of water in concrete pore by molecular dynamics simulation using LAMMPS

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ABSTRACT

As for the communication between concrete and the particles, the surface shows Cl⁻ shock and Na adsorption. With expanded particle focus, the solid adsorption capacity for Cl⁻ is upgraded as a result of a detailed overview of the dynamic molecular simulation studies examining the chloride diffusion coefficient. Different characteristics of the diffusion process, including molecular models, system-size effects, temperature, and pressure conditions, and the type of protection, are discussed. This paper focus on Molecular Dynamic Simulation to determine the diffusion coefficient of chloride ion and water molecules in concrete. The diffusion coefficient for NaCl salt obtained $6.60178 \times 10^{-10} \text{m}^2/\text{s}$ and the diffusion coefficient for CaCl₂ salt obtained $7.29305 \times 10^{-10} \text{m}^2/\text{s}$. So, the average chloride diffusion coefficient $6.9475 \times 10^{-10} \text{m}^2/\text{s}$. Diffusion coefficient obtained from graph $5.562 \times 10^{-10} \text{m}^2/\text{s}$. Diffusion coefficients for water molecules for NaCl solution are $6.125 \times 10^{-10} \text{m}^2/\text{s}$, $6.85 \times 10^{-10} \text{m}^2/\text{s}$, $1.044 \times 10^{-10} \text{m}^2/\text{s}$, $8.525 \times 10^{-10} \text{m}^2/\text{s}$, $6.25 \times 10^{-10} \text{m}^2/\text{s}$. Diffusion coefficient of water molecules in CaCl₂ solution are $4.5 \times 10^{-10} \text{m}^2/\text{s}$, $6.725 \times 10^{-10} \text{m}^2/\text{s}$, $1.254 \times 10^{-10} \text{m}^2/\text{s}$, $7.725 \times 10^{-10} \text{m}^2/\text{s}$, $1.3 \times 10^{-10} \text{m}^2/\text{s}$. Average value obtained for water molecule diffusion are $4.545 \times 10^{-10} \text{m}^2/\text{s}$, $7.4062 \times 10^{-10} \text{m}^2/\text{s}$ and $1.149 \times 10^{-10} \text{m}^2/\text{s}$. This diffusion of chloride effects the binding of water in concrete pore.

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1. Introduction

Cement is the most consumed substance on construction purpose. On average three tons of concrete are consumed annually by every human being living on Earth. Cement is one of the most widely accepted materials in the world. Concrete is the second most. The cement industry accounts for almost 5-7% of global carbon dioxide (CO₂) emissions. Despite its other pollution, the industry is the third-largest producer of greenhouse gasses in the world. Besides, cement production is the third-largest energy consumer sector. On the other hand, in hostile conditions such as seawater, the Cl⁻ ions may enter the cement paste and contribute to the deterioration of the reinforcement (Arya and Xu, 1995; Page et al., 1986). It has a harmful effect on the durability of the structure.

Diffusion is a very important parameter such that sometimes specification is presented with regards to

diffusion (Honorio et al., 2019). As Chloride diffusion water diffusion is also an important parameter. It has an inverse relationship with strength of concrete. High strength concrete has a lower diffusion coefficient, where low strength concrete has a higher diffusion coefficient (Balakrishna et al., 2018). Moreover interaction between water and C-S-H gel may have a substantial effect on the cohesion force (Bonnaud et al., 2012; Lesko et al., 2001).

To interpret the diffusion process in various length scales, it is important to explore the origin of the property at the molecular level. Calcium silicate hydrate (C-S-H) is the fundamental hydration result of concrete powder and water. Concrete hydrates have a multi-scale permeable structure that contains capillary pores and gel pores (Ma and Li, 2013). Transport of the water in the permeable medium has an incredible impact on the strength, creep, shrinkage, and compound and actual

reactivity of concrete glue. From one viewpoint, ecological changes, for example, the temperature, moistness, and stacking, can bring about water content varieties in C-S-H gel. Then again, in an aggressive environment, for example, ocean water, the Cl^- particles can infiltrate the concrete glue and lead to the erosion of reinforcement (Arya and Xu, 1995; Page et al., 1986). It detrimentally affects the solidness of the structure.

To decipher the dissemination system at various length scales, it is important to explore the inception of the property at a sub-atomic level. The ^1H NMR test explored the properties of water in the nano-pores of C-S-H gels (Wang et al., 1998) and the quasi-elastic neutron scattering (QENS) method (Bordallo et al., 2006).

The physical and structural properties of water can vary substantially between bulk water and near surface water as surfaces tends to disturb fluid structure up to a certain atomic diameter from surface. This phenomena can be used to understand the chemical properties of mineral pore surface. However even after various studies and methods have been carried out to find the difference, it's still not completely understood. Here molecular dynamics can help to accelerate the advancement of understanding (Kalinichev et al., 2007). Although previous researchers had obtained various creative methods molecular dynamics can be more helpful in understanding what happens at atomic level. It is a well suited tool to understand specific ion effects in aqueous solution. It was also has been extensively used in past to understand this phenomena (Honorio et al., 2019).

In this study tobermorite 11A is used as cement molecule as it has similarities with C-S-H which is the building block of cement paste. As the modeling of micropore is both time consuming and not practical for computer based atomistic simulation. Modelling micropore can solve this problem as well as give accurate result. So a pore size of 60Å is chosen which was a gel pore and can give very accurate result.

2. Method and Methodology

2.1. Simulation model

Methods for crystal analogues are commonly used to model C-S-H gel. In this analysis, Hamid's 11Å tobermorite structure (Hamid 1981) is considered. A few modifications, such as adding calcium ions and hydroxyl groups to the tobermorite structure, must be done to have a crystal stone structure equal to the actual structure of C-S-H gel (Kurczyk and Schwiete, 1962). Inclusion of tobermorite between portlandite sheets (Kantro et al., 1962), integration into the portlandite system of silicate monomer groups (Shpynova et al., 1967), consideration of some calcium ions and hydroxyl groups in the structure and interlayer spaces between tobermorite silicate chains (Taylor and Howison, 1956) the elimination of such bridging tetrahedral silicon groups and the insertion of interlaminar calcium ions (Garboczi and Bentz, 1992). No improvement in the replication model has been considered in this paper and particular forms of previously described crystal are studied. For the evaluation of

complex properties such as surface interactions and transportation characteristics, it is entirely required to reveal substrates at the recreation finishes enclosing and a nanopore the supercell core that combines the anion and cation fluid structure. Previous experts for tobermorite have revised this technique (Kalinichev and Kirkpatrick, 2002; Buenfeld et al., 2014) and other hydrates such as portlandite, Friedel's salt, AFM phases, Aft phases, brucite, and gibbsite (Yu and Kirkpatrick, 2005; Kalinichev et al., 2007).

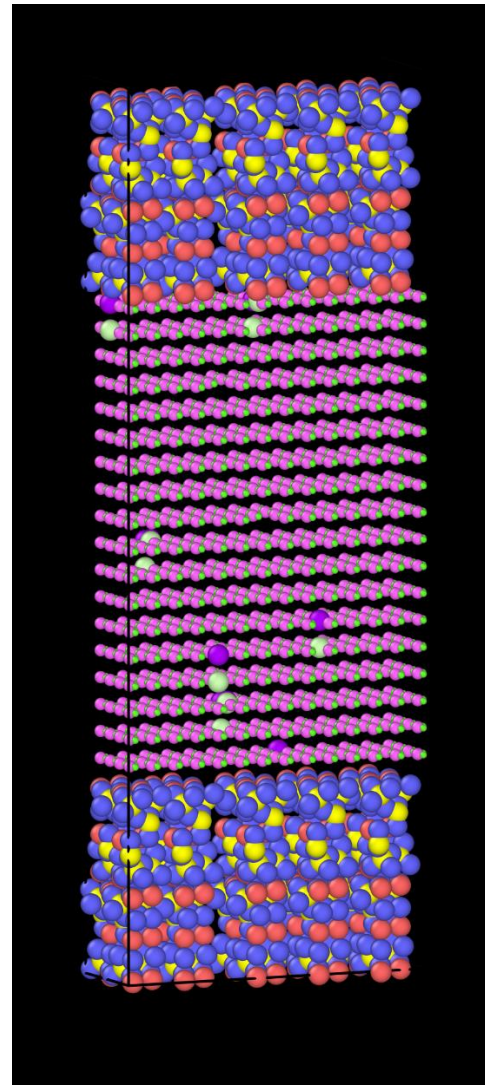


Fig. 1. Snapshot of the simulation cell captured by OVITO (purple represents Oxygen atoms, green represents Hydrogen, light green represents Chloride ions, violet represents Sodium, red represents Calcium, Blue represents Silicon).

2.2. Simulation settings

Molecular dynamics (MD) is usually used at the atomistic level to provide a superior understanding of matter and individual interactions between particles or atoms and to determine specific material properties (Gopalakrishnan et al., 2011). MD is ideal for measuring time-subordinate properties, such as the coefficient of diffusion.

The Molecular Dynamics simulation methodology was performed using LAMMPS in this analysis. The diffusion coefficient of chloride ions is variable for various pore sizes. For this simulation cell model, the temperature was 273°C (300°K). For the simulation the NVT ensemble was used, which was a canonical ensemble, where the number of particles which is represented by N , the volume of the system which is represented by V , and the temperature of the system which is represented by T were conserved and rest of the variables were allowed to vary to compensate the changes that were applied to the model. To run the model, the initial relaxation time was 500ps, as the simulation was run for 2200 ps. The thermostat that conserved the energy was both exothermic and endothermic. For the analysis of the input file that was provided to LAMMPS time step was set to 1fs enabling calculation to be sufficiently accurate. The dump file was generated by extracting the atomic positions and velocities for every 100time steps or 100 fs, enabling the dump file to contain 220,000 different atomic positions and velocities which was used to visualize in a MD visualization software called OVITO, and later for calculating the required data. Here the results

were statistically reliable as the simulation was run for 2200ps or 2.2ns, which is well above 0.5 ns. On top of that the number of atoms were large enough and the super-cell size was big enough to provide further reliability (Buenfeld et al., 2014).

It is important depending on the point of interest of MD simulation. Diffusion coefficient, the force field and potential as well as the atomic positions. The same can be said for the case salt properties on LJ potential parameters such as σ and ϵ (Table 1). Running the model using a MD software certain values of these σ and ϵ will give the most accurate results such as solubility, alkalinity and acidity of the salt water solution. Same can be assumed for the water molecule. The molecular trajectory of the water, the motion of the water in the super-cell, the transportation capacity of water etc. will depend heavily upon these potential parameters.

In this study the Sodium Chloride (NaCl) and the water molecule were ensured to be stable in their crystal structure.

This parameter shown in the above table are used for the simulation. Here, 1Å is 100 Pico meter and e is the charge of single electron or proton which is 1.602×10^{-19} C.

Table 1. Lennard Jones potentials.

Model	ϵ (kJ/mol)	Σ (Å)	q (e)	m (g/mol)
Na	0.600	2.440	+1	22.9897
Ca	0.540	3.270	+1	40.0780
Cl	0.054	4.830	-1	35.4530
H	0.000	0.000	+0.4236	1.00794
O	0.650	3.166	-0.84720	15.9940

3. Data Analysis and Calculations

To find the diffusion coefficient of the model, a kinetic study was used. It is useful to find that there are three procedures of determination of the diffusion coefficient. The first way to find the coefficient is by using the velocities of the ions (or molecules). In this method, the diffusion coefficient can be obtained by the integration of the Velocity Autocorrelation Functions (VAF). A good example of this is the Green Kubo relations (Haile 1992). The second method is Force Autocorrelation which is used to calculate the diffusion over the energy barrier and uses the fluctuation-dissipation system. In this case, the molecules are set where it is desired and the force that is acting on them in time, $F(t)$ is taken. In this method the diffusivity is nothing but the correlation of time. The last method uses the positions of the molecules and by the information the Mean Squared Displacement or MSD is obtained to get the diffusion coefficient. The end result given by each method is more or less the same and any one of them can be used depending on what the end goal is. In this study, LAMMPS is used to calculate the diffusion coefficient using the third method or MSD.

3.1. Diffusion coefficient from MSD (NaCl)

The diffusion of the water was studied first. For this The Mean Square Displacement (MSD) values were obtained from LAMMPS. Upon starting the initial positions $r_i(0)$ were set to all particles by using the MSD. Then the displacement for each particle was calculated with respect to their positions. Here Einstein diffusion coefficient formula can be applied, which can be expressed as follows r_i .

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

$$D = \lim_{t \rightarrow \infty} \left(\frac{\langle (r(t) - r(0))^2 \rangle}{n} \right) \quad (2)$$

where r_i is the location of a particle at step i , and N is the number of frames dumped from the MD. The diffusion coefficient is D , t_0 is the initial time of simulation and d is the dimensionality of the system.

Fig. 2 is a graph of MSD values that were obtained from LAMMPS for Chloride ions for Sodium Chloride solution. It should be noted that the values are only after the simulation had been run, so the initial relaxation time is not present in the graph.

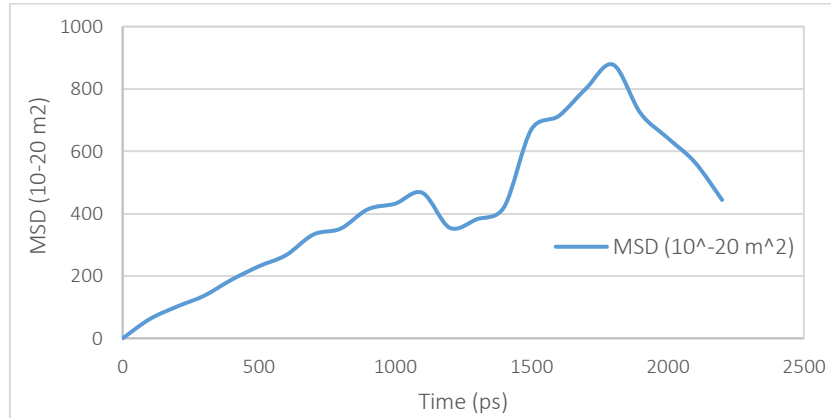


Fig. 2. MSD vs. time graph for Chloride ions in NaCl solutions.

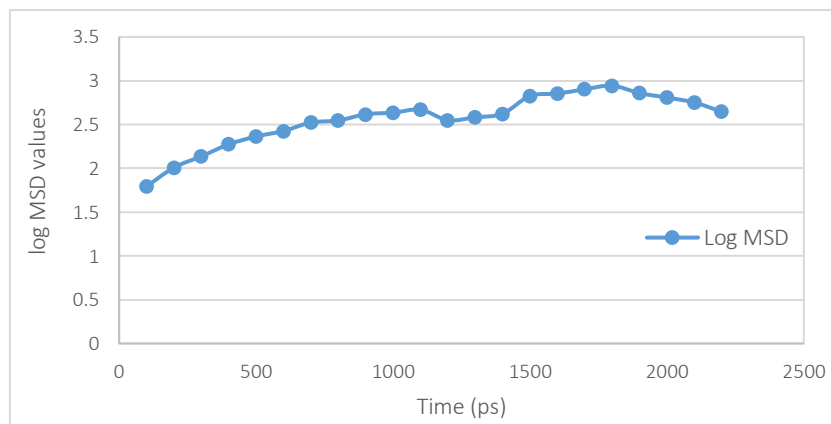


Fig. 3. Log MSD vs. time graph for Chloride ions in NaCl solutions.

In Einstein's formula, the dimensionality d is taken as 3 for three dimensional systems. For $d=3$ the formula can be simplified as:

$$MSD = 6Dt \quad \text{or} \quad D = \frac{MSD}{6t} \quad (3)$$

Here D , MSD and t are all in SI units. The unit style that is used in LAMMPS is real, which means MSD is in \AA^2 , D is in $\text{\AA}^2/\text{s}$, and time is in picoseconds. So, they were converted in SI units by $1\text{\AA} = 10^{-10} \text{ m}$, $1\text{ps} = 10^{-12} \text{ seconds}$.

3.2. Diffusion coefficient from MSD (CaCl_2)

As mentioned earlier for Sodium Chloride and Calcium Chloride simulation models were built separately and calculated separately. The calculation of the diffusion coefficient for Chloride ions in Calcium Chloride solution is carried out in the same way. First, the MSD values were extracted from the LAMMPS simulation and the values were put in a graph (Fig. 4).

After that, the log values of the Cl ions were put into the graph in the same way (Fig. 5).

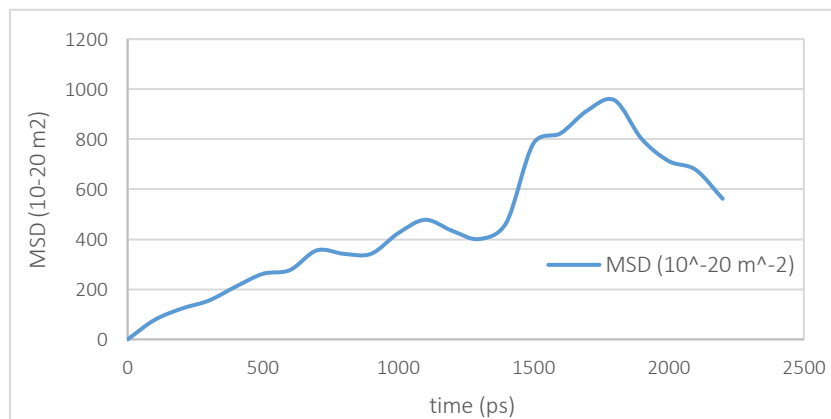


Fig. 4. MSD vs. time graph for Chloride ions in CaCl_2 solutions.

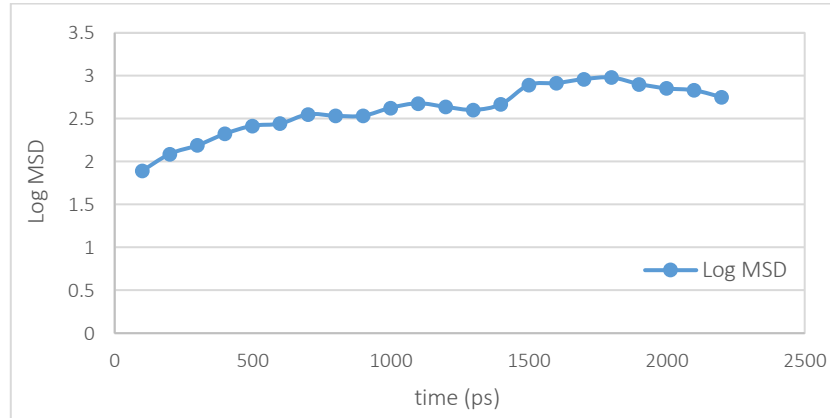


Fig. 5. Log MSD vs. time graph for Chloride ions in CaCl_2 solutions.

Using Einstein's formula, the diffusion coefficient of the Chloride ions in Calcium Chloride is calculated.

3.3. Diffusion coefficient of water molecule

The 992 water molecules were divided into two major groups. They are the intermolecular water molecules and the intra molecular water molecules. Their MSD values and diffusion coefficient were calculated using

LAMMPS and Einstein's formula respectively. First, the MSD values from LAMMPS were plotted in a graph which was also done for the Chloride ions (Fig. 6).

To calculate the diffusion coefficient of water the MSD values obtained from LAMMPS were used. But before that from the position of each atom, the density of the water molecule was calculated. The position of the water molecule is contained in the dump file that was created after simulating LAMMPS.

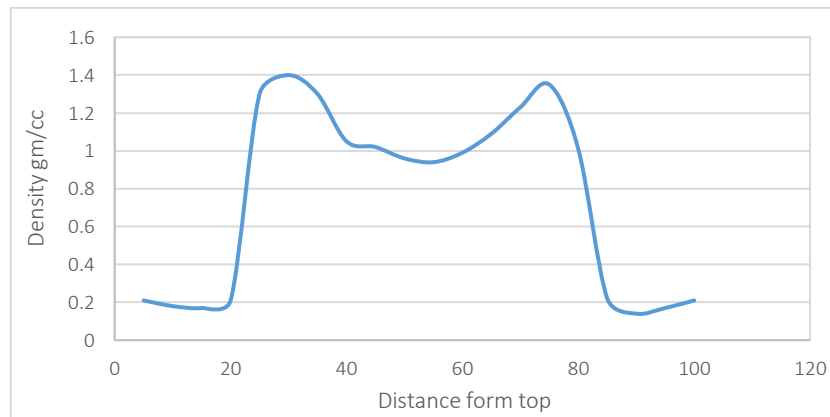


Fig. 6. Density of water vs. distance from top in z-axis.

As mentioned earlier the total dimension in the z-direction is 100Å . The top and bottom 20Å is occupied by tobermorite atoms. Rest of the 60Å is the pore space in the simulation model, which contains NaCl or CaCl_2 solution. From counting the number of each atom in a small local region the density of the water at that particular region can be obtained. The values were automatically obtained from LAMMPS.

The top part of the graph shows the water molecules were densely concentrated near the substrates. It shows that the middle part had a density of water of about 1 gm/cc . It indicates that for the middle one third the value of the density did not change from its initial value. If we look closely at Fig. 6, we can notice that the values of distribution mirror from the middle centreline of the nanopore, which makes it symmetrical along the middle of the pore. After calculating the diffusion coefficient values from MSD that were provided by LAMMPS.

4. Result and Discussion

4.1. Diffusion coefficient of chloride ions

From Eq. (3) the values of diffusion coefficient were calculated from MSD values. The results thus obtained for Chloride molecules for different time steps. The values were averaged to get the diffusion coefficient of the Chloride ions for both salts. The value of diffusion coefficient obtained for NaCl salt solution is $6.60178 \times 10^{-10} \text{ m}^2/\text{s}$ and for CaCl_2 solution is $7.29305 \times 10^{-10} \text{ m}^2/\text{s}$. And the diffusion coefficient obtained by averaging these two values is $6.9475 \times 10^{-10} \text{ m}^2/\text{s}$. The diffusion coefficient values obtained by previous researchers are $1.07 \times 10^{-9} \text{ m}^2/\text{s}$ for cement paste (experimental) (Pivonka et al., 2004) and 7.097×10^{-10} for Hamid's 11Å tobermorite (Behnam and Amir, 2017). The values obtained in this study is thus satisfactory with previous researchers.

Figs. 7 and 8 show the comparison of MSD values for NaCl and CaCl₂ solutions. From the figures we can see that the MSD values are almost close for both salts. So, their diffusion coefficient should also be similar, which is true for the values obtained in this study. The values are only 5% apart for two types of salt. Hence, it can be said that the diffusion coefficient of Chloride ion does not matter too much on the type of salt.

This diffusion coefficient is obtained from the MSD values by using Einstein's formula. It can also be calculated from the slope of the log MSD graph. The slope of the log-MSD graph is shown in Fig. 8. From the slope the obtained diffusion coefficient is $5.562 \times 10^{-10} \text{ m}^2/\text{s}$. This is almost similar to the value obtained by using Einstein's formula.

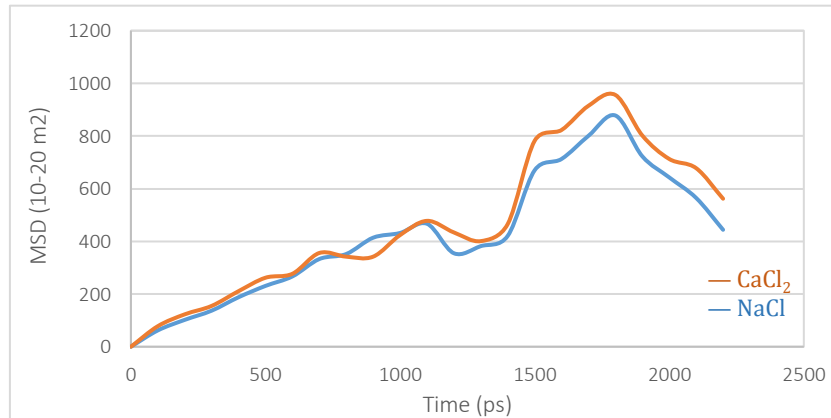


Fig. 7. MSD vs time graph for Chloride ions in NaCl and CaCl₂ solutions.

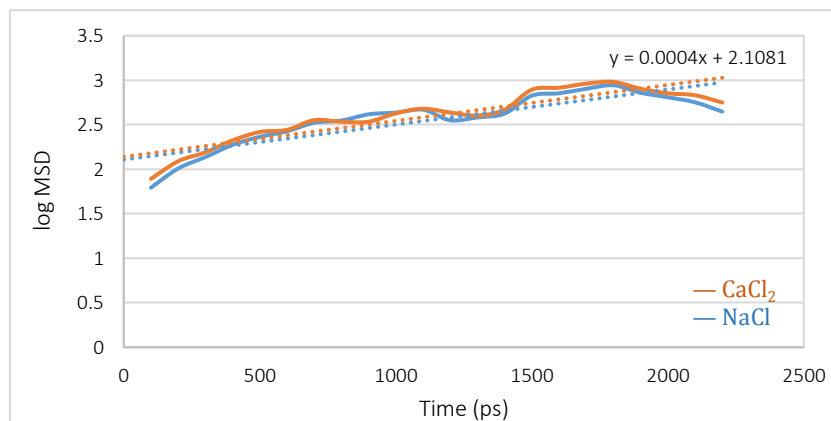


Fig. 8. Log MSD vs. time graph for Chloride ions in NaCl and CaCl₂ solutions.

4.2. Diffusion coefficient of water molecule

The water molecules in the simulation model can be divided into three categories. The first is Intra-molecular water molecules, which is in the tobermorite layer. Such water molecules are entrapped by the tobermorite molecules and have very little freedom to move. The second category is the water molecules near the surface of the tobermorite layer. This represents the inner surface of a concrete nano-pore. Here, the water molecules are subjected to the adsorption by the electrostatic interaction with tobermorite molecules. So, their movement is supposed to be restricted by a bit. The third category is the water molecules which are situated in the within the region equal to the height of one third of the pore space from either side of the centreline. Here, the water molecules should behave just like the free water molecules because the distance from the tobermorite layer is too high to be affected by the adsorption. To be free from the

adsorption the distance of the water molecule should be at least 3 times the radius of the water molecule, which is roughly 8-10Å (Kalinichev et al., 2007), which is true for this category.

In Figs. 9 and 10, the variation of diffusion coefficient values and their initial positions in the primary configuration is shown. The diffusion coefficient of intra-layer water molecules are at the beginning and end part of the graph in Figs. 9 and 10. The curve line is gotten by the average value of the diffusion coefficient for specific locations. Water molecules can be grouped into two types. They are the interlayer and intralayer. The interlayer molecules can be further divided into two groups. They are molecules near the pore surface and molecules near the middle 1/3rd of the pore.

For the Intra-space of NaCl solutions diffusion coefficient of water molecules at top is $6.125 \times 10^{-11} \text{ m}^2/\text{s}$ and for molecules of waters at bottom is $6.25 \times 10^{-11} \text{ m}^2/\text{s}$. And for CaCl₂ solution this value is $4.5 \times 10^{-11} \text{ m}^2/\text{s}$ for top

layer and $1.3 \times 10^{-11} \text{ m}^2/\text{s}$ for bottom layer. Average diffusion coefficient is $7.4685 \times 10^{-11} \text{ m}^2/\text{s}$, which is close to previous researches. The previous researches show that the intralayer diffusion coefficient are $5.0 \times 10^{-11} \text{ m}^2/\text{s}$ (Kalinichev et al., 2007) and $1.4 \times 10^{-11} \text{ m}^2/\text{s}$ (Yoon and Monterio, 2013). The diffusion coefficient is relatively

small in the intralayer spaces, mainly due to the water molecules that are present in here is a bit like crystal. They behave mostly like solid particles and are in a harmonic motion due to the force that was acted upon them, as they were trapped between the silicate chains as well as having a very powerful Hydrogen bond.

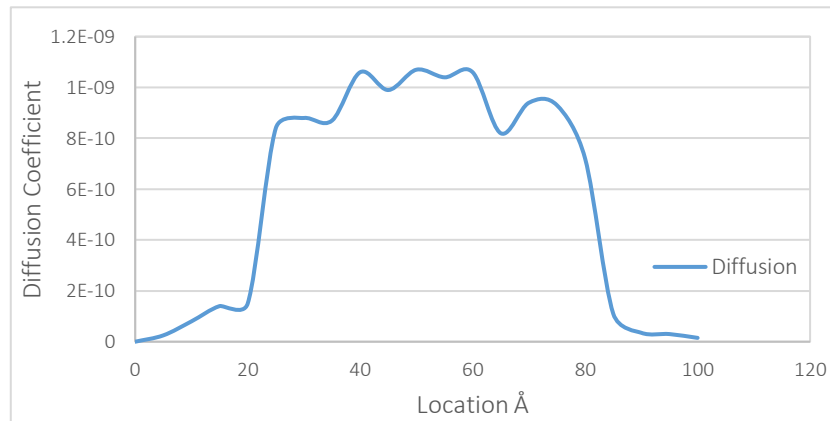


Fig. 9. Diffusion coefficient of water molecules in NaCl solution with respect to distance from the top.

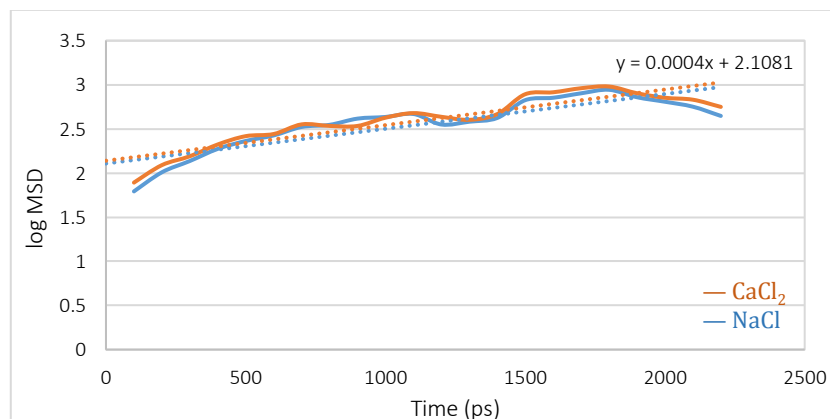


Fig. 10. Log MSD vs time graph for Chloride ions in NaCl and CaCl₂ solutions.

The interlayer part that is composed of two groups-near surfaces and near middle one third region.

For near surface water molecules in NaCl solution the diffusion coefficient at top is $6.85 \times 10^{-10} \text{ m}^2/\text{s}$ and $8.525 \times 10^{-11} \text{ m}^2/\text{s}$ at bottom. For CaCl₂ solution these values are $6.725 \times 10^{-10} \text{ m}^2/\text{s}$ at top and $7.725 \times 10^{-10} \text{ m}^2/\text{s}$ at bottom. The average value is $7.4685 \times 10^{-11} \text{ m}^2/\text{s}$. The values obtained by previous researchers are $5 \times 10^{-11} \text{ m}^2/\text{s}$ (Kalinichev et al., 2007) and $1.4 \times 10^{-10} \text{ m}^2/\text{s}$ (Yoon and Monterio, 2013). This shows the obtained value in this study is close with previous researches.

For the molecules near the middle 1/3rd of the model is about $1.14 \times 10^{-10} \text{ m}^2/\text{s}$ to $1.23 \times 10^{-10} \text{ m}^2/\text{s}$ in NaCl and CaCl₂ respectively. The values obtained by the previous researches for free water molecules are $4.13 \times 10^{-10} \text{ m}^2/\text{s}$ by the SPC model (Buenfeld et al., 2014). The values indicate that the middle 1/3rd water molecules are less affected by the tobermorite surfaces. This phenomenon enables them to diffuse more freely and their distance is larger compared to other water molecules and close to the free water molecule.

5. Conclusions

Cement is the most consumed substance for construction purposes. On average three tons of concrete are consumed

Following conclusions were made from the results and observation of the study:

- The diffusion coefficient of Chloride ion is hardly affected by the type of salt. It is shown that the result obtained for one type of Chloride solution can be easily matched by other type of Chloride solution. This study shows only 5% difference between two types of salt. So, effect of Chloride ion ingress will cause equal effect for a cement paste, regardless of the salt. This statement is also supported by previous researchers, as the values matches with their.
- Surface binding of the water molecules have a bigger effect on the transportation of the water molecules in the cement nano-pore. The study shows that near surface water molecule has diffusion coefficient less than the molecules near middle by a factor of 36%.

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