

Effects of Aluminum Incorporation in Tobermorite Structure on Chloride Diffusion: A Molecular Dynamics Simulation Study

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Received: 25 Mar. 2018;

Revised: 24 Oct. 2019;

Accepted: 26 Nov. 2019

ABSTRACT: In this paper, the effects of different aluminum to silicon ratios in silicate chains of calcium silicate hydrates (C-S-H) are evaluated on the diffusion coefficient of chloride ions by molecular dynamics method. Tobermorite is a crystalline phase that is used for studying C-S-H properties in nano scale, because of its analogous chemical composition to C-S-H. Aluminum incorporation in C-S-H and the formation of calcium aluminosilicate hydrates (C-A-S-H) is due to both of hydration of tricalcium aluminate (C₃A) in portland cement and aluminum oxides in pozzolans. There exist different Al/Si ratios in the tetrahedral chains of C-A-S-H depending on available aluminum oxides in cementitious raw materials. In order to compare the simulation results with previously-published experimental researches on cement pastes, a novel method is introduced here to calculate Al/Si ratio in tetrahedral chains of C-A-S-H using pozzolan replacement ratio in cementitious paste. MK (metakaolin) and FC3R (Fluid Catalytic Cracking Catalyst Residue) are the pozzolans that are used to validate the obtained results in this paper. Results showed that diffusion coefficients of chloride ions in C-A-S-H decrease by Al/Si ratio increasing in the tetrahedral chains as it was observed experimentally in previous researches.

Keywords: Aluminum, C-A-S-H, Chloride Diffusion, C-S-H, Molecular Dynamics, Pozzolan, Tobermorite.

INTRODUCTION

The chloride ion is one of the most harmful ions that enters through pores of reinforced concrete elements. Chloride ions concentration, as well as the existence of oxygen and humidity, are the main reasons of corrosion of steel bars in reinforced concrete structures (Bertolini et al., 2013). Corrosion extremely reduces the lifetime of concrete structures (Tarighat and Zehtab, 2016).

Chloride ions easily penetrate into ordinary portland cement pastes through gel pores. The best way to prevent chloride penetration into interior parts of cement paste could be a reduction of permeability of the cementitious material elements. It is achievable by increasing the quality of cement paste construction and reducing water to cement ratio (Powers et al., 1959). Apart from physical aspects of cement paste, the chemical composition of mix design has

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major effects on diffusion of chloride ions. C-S-H does not have much of the ability to uptake free chloride ions while aluminate phases (AFm) can accommodate them, significantly (Balonis et al., 2019). It must be noted that AFm phases contain about 15% of cement constituents and they cannot uptake the high contents of free chloride ions in ordinary cement pastes.

It is shown experimentally that using supplementary cementitious materials in cement paste mix design could decrease diffusion of chloride ions in comparison with ordinary Portland cement pastes (Caneda-Martínez et al., 2018, Madani et al., 2016; Madani and Kooshafar, 2017; Tadayon et al., 2016; Farahani et al., 2018; Yang et al., 2015). It has been shown that diffusion coefficients of chloride ions in high alumina cement (HAC) pastes (Ann et al., 2010), mortars containing FC3R and fly ash (Zornoza et al., 2008), cementitious pastes containing fly ash (Zhang and Ye, 2015), blast furnace slag (Zhang and Ye, 2015) limestone powder (Zhang and Ye, 2015), MK (Shekarchi et al., 2010; Ramezani-pour and Jovein, 2012) and silica fume (Ding and Li, 2002) are lower than ordinary portland cement (OPC) pastes.

Durability improvement of pozzolan-included cementitious pastes is mainly due to pore refinement in cement paste that contains pozzolanic materials. Porosity reduction causes permeability of paste to decrease and it protects cementitious pastes against destructive chemical actions (Mehta and Monteiro, 1993). It is proved that formation of calcium-aluminosilicate-hydrates (C-A-S-H) is another reason for better durability of pozzolan-included cementitious pastes in the case of chloride diffusion. These hydrates bind Cl ions and it causes the diffusion coefficient of chloride ions to be decreased (Ukpata et al., 2019; Zhang et al., 2019). When chloride ions face with hydrates containing aluminum and calcium atoms,

they would be bound. Chloride binding is due to the formation of calcium chloroaluminate hydrate or Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$). Friedel's salts prevent chloride ingress through the cementitious paste. They postpone the corrosion process of reinforcing bars because of their delayer character for reaching of chloride ions to steel bars surfaces (Jones et al., 2003). However, it is worth noting that Friedel's salt is not a stable product. It can decompose so that bound chloride ions can release again if the cement paste deals with carbonation or sulfate attack, afterward (Justnes, 1998).

Many researchers proved experimentally that aluminum incorporation in cement paste could affect diffusion coefficient of chloride ions. Regardless of the publishing several empirical types of research in the literature, atomistic simulation studies are needed in this field. Using nanoscale simulation, it is possible to study the structure of C-S-H and its properties precisely. Dynamic properties of materials such as diffusion are time-dependent quantities and they could be simulated using Molecular Dynamics (MD) (Leach, 2001). One can calculate diffusion coefficients of aggressive ions such as chloride ions using trajectories of ions during simulation time (Zehtab and Tarighat, 2016; Zehtab, 2017).

Aluminum incorporation to C-S-H structure and C-A-S-H formation could be also simulated using MD. Aluminum can substitute in two different positions: replacement for silicon atom in silicate chain (bridging site or paired site) or interlayer calcium atoms (which it has low possibility) (Abdolhosseini Qomi et al., 2012). Most of the researchers reported that aluminum would be preferentially substituted in the bridging site, especially in low Al/Si ratios (Abdolhosseini Qomi et al., 2012; Manzano Moro, 2014). Bridging silicon is energetically less stable than non-bridging silicon atoms

and therefore aluminum prefers to be substituted with bridging silicon in order to build a more stable structure for C-A-S-H (Faucon et al., 1997). Substituted aluminum with interlayer calcium can make a cross-linkage between bridging silicon atoms in adjacent layers (Abdolhosseini Qomi et al., 2012).

Although aluminum substitution in interlaminar space of C-S-H can highly improve mechanical properties of C-S-H, most of the researchers rejected this assumption based on their experimental observations. They claimed that these pentacoordinated and hexacoordinated aluminates could be formed due to aluminate phase growth on the surface or in the interlayer space of C-S-H (Richardson et al., 1993; Andersen et al., 2006). Mechanical properties of C-A-S-H such as stress-strain relation and consequently Yang's modulus and tensile strength can be found using molecular dynamics simulation for different Al/Si ratios (Hou et al., 2015; Geng et al., 2017). Evaluation of C-A-S-H properties using molecular simulation is relatively new field and durability-related issues such as diffusion coefficient of chloride ions are not focused using MD in the literature.

In this research paper, aluminum substitution in silicate chain of 14 Å tobermorite (Merlino et al., 1999) is simulated. Molecular dynamics is implemented to study diffusion process of chloride ions through a nanopore within tobermorite layers. Tobermorite is a mineral crystal that is chosen due to its similarity to C-S-H structure and atomic configuration (Al-Ostaz et al., 2010; Hajilar and Shafei, 2015; Zehtab and Tarighat, 2016). Diffusion coefficients of chloride ions are calculated for different Al/Si ratios: Al/Si = 0, 0.2, 0.5, 1, 2, 5 and ∞ . Aluminum content in the simulation model is changed to construct different simulation models: primary structure (C-S-H, Al/Si = 0), C-A-S-H (Al/Si = 0.2, 0.5, 1, 2 and

5) and finally C-A-H (Si/Al = 0). It is required to convert pozzolan-to-cementitious materials ratio into Al/Si ratio in tetrahedral chains of C-A-S-H for comparing simulation results with experimental outputs. In this paper, a formula is proposed to find Al/Si ratio in silicate chain of C-A-S-H based on the chemical composition of consumed pozzolan in the cementitious paste. Diffusion coefficient variation of chloride ions is verified by experimental results of previous researchers. It has been shown that the trend of decreasing in diffusion coefficient by increasing in aluminum content was approximately similar in our simulation study and experimental data.

MATERIALS AND METHODS

Aluminum Substitution

Aluminum ions could be found in the structure of cement hydrates when portland cement has a high volume of C3A phases or cement paste includes pozzolanic materials with high Al₂O₃ phases. After cement hydration, some parts of aluminum incorporated in the composition of cement paste precursors would appear in silicate gel and the other would form Afm (alumina ferric oxide mono-sulfate, monosulfoaluminate) and Aft (alumina ferric oxide tri-sulfate, trisulfoaluminate) crystalline phases. These crystalline phases would be formed separately in the pores and they are not related to any case of ion substitution. In this paper, it is focused on aluminum substitution in C-S-H gel and formation of aluminosilicate calcium hydrate (C-A-S-H), consequently. Silicon substitution by aluminum would unbalance electrical neutrality of simulation cell due to the difference between numbers of electrons in the valence shell of aluminum and silicon (Faucon et al., 1999a).

Aluminum and silicon belong to the group 13 and 14 of periodic table and they have 3 and 4 electrons in their valence shell,

respectively. Each Al-substitution leads to create one more negative charge than electrical charge of the neutral state of simulation cell. Previous researchers have proposed some electrical neutralization methods. The extra negative charge could be counterbalanced by ions Ca^{2+} , Na^+ , H^+ , etc. Manzano and Qomi et al. suggested using Na^+ for playing a key role counterbalancing the charge (Abdolhosseini Qomi et al., 2012; Manzano Moro, 2014). Charge balance for bridging site or paired site could be provided by interlayer Ca^{2+} , Na^+ , or H^+ or cross-linkage between aluminum ions in adjacent chains (Sun et al., 2006). Hou et al. (2015) simulated substitution of 2Si^{4+} by 2Al^{3+} in the tetrahedral chain and one interlayer Ca^{2+} .

Faucon et al. (1997, 1998, 1999a,b) based on their experimental observations proposed to protonate non-bridging oxygen atoms by H^+ (Al-OH groups) for compensation the extra charges or to neutralize by the accommodation of sodium in the interlayer space. Based on the previous works, in this research silicon atoms have been substituted by aluminum atoms in bridging sites preferably. For high Al/Si ratios, all of the bridging silicon atoms have been substituted by aluminum atoms and additional aluminum atoms have been placed on pairing sites in the tetrahedral chain instead of silicon atoms. Each aluminum atom has been substituted in the tetrahedral chain and one of the non-bridging oxygen atoms would be protonated by H^+ to form Al-OH group.

Diffusion Coefficient Estimation

There are several methods for estimating diffusion coefficient of different ions and molecules. The simplest method with a low computational cost and rare numerical problem is mean squared displacement (MSD) method. Well-known Einstein formula demonstrates that mean squared displacements resulting from molecular motion of particles have a relation with

diffusion coefficient of those particles (Einstein, 1956). To conduct this method in this paper, displacement data of chloride ions must be extracted from each simulation model. Diffusion coefficient (D) will be obtained for each chloride ion by calculating mean squared displacements (MSDs) and implementation of Einstein formula (Einstein, 1956):

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle \Delta \vec{r}(t)^2 \rangle}{t} = \frac{MSD}{2dt} \quad (1)$$

where Δr , d , and t : are displacement of specific ion (or molecule), the dimensionality of the simulated system (value of 3 for the three-dimensional system) and time step, respectively.

Simulation Model

In this paper, molecular dynamics method was implemented to carry out the simulation of silicon substitution by aluminum in the tetrahedral chain of C-S-H. Tobermorite 14\AA (Bonaccorsi et al., 2005) was chosen to simulate C-S-H atomistic model due to their similarity in structure and compositions. It is a common procedure that analogous crystalline mineral materials such as tobermorite would be investigated for studying C-S-H properties (Hou et al., 2014; Qomi et al. 2014; Zehtab and Tarighat, 2016). The space group of tobermorite 14\AA is B11b with monoclinic crystal system and its unit cell lattice constants are given in Table 1 (Bonaccorsi et al., 2005). The unit cell of tobermorite 14\AA is shown in Figure 1.

As it is shown in Figure 2, there is a pore with a width of 5 nm between two substrates constructed using tobermorite crystals. Each of two substrates was produced by $2 \times 3 \times 1$ unit cells of tobermorite 14\AA which were placed side by side. Due to modeling a specific size for nanopore that is greater than 5 angstroms and smaller than 100 angstroms, the modeled nanopore could be considered as a gel pore

(Mindess et al., 2003). Moreover, nanopore size must be smaller than 10 nm to properly study chloride ions diffusion in cementitious hydrates (Pivonka et al., 2004). To evaluate the process of diffusion, an aqueous solution must be modeled in the pore. The density of this aqueous solution should be considered about 1 g/cm³ so that ambient conditions to be satisfied (Hou and Li, 2014). To reach this

purpose 493 water molecules were simulated in the supercell. Cl⁻ and Na⁺ ions were provided in aqueous solution to assess diffusion process. Seven different models were considered to evaluate the incorporation of different aluminum contents in C-S-H hydrates. Properties of these models are presented in Table 2 and their supercells are shown in Figure 2.

Table 1. Unit cell lattice constants of tobermorite 14Å

	a (Å)	b (Å)	c (Å)	α	β	γ
tobermorite 14Å	6.73	7.42	27.98	90°	90°	123.25°

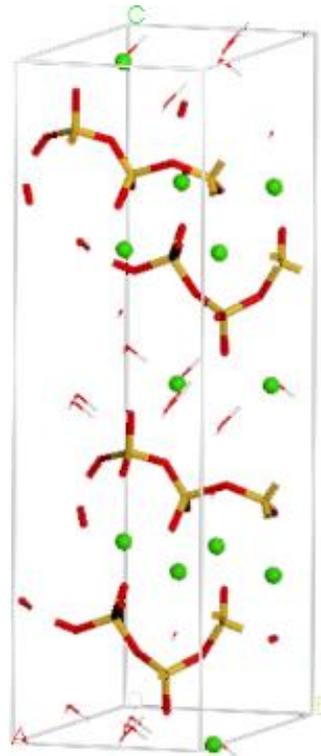


Fig. 1. The unit cell of tobermorite 14Å crystal. Silicon, oxygen, hydrogen, and calcium (shown in yellow, red, white and green colors, respectively). Tetrahedral chains are shown using sticks, water molecules presented by lines and calcium ions illustrated by balls

Table 2. Simulated models' properties

Model name	Al/Si	Number of Al and Si atoms in supercell		Number of Al atoms in each position of substitution	
		Al ³⁺	Si ⁴⁺	Bridging	Pairing
CSH	0	0	144	0	0
CASH0.2	0.2	24	120	24	0
CASH0.5	0.5	48	96	48	0
CASH1.0	1.0	72	72	48	24
CASH2.0	2.0	96	48	48	48
CASH5.0	5.0	120	24	48	72
CAH	Si/Al = 0	144	0	48	96

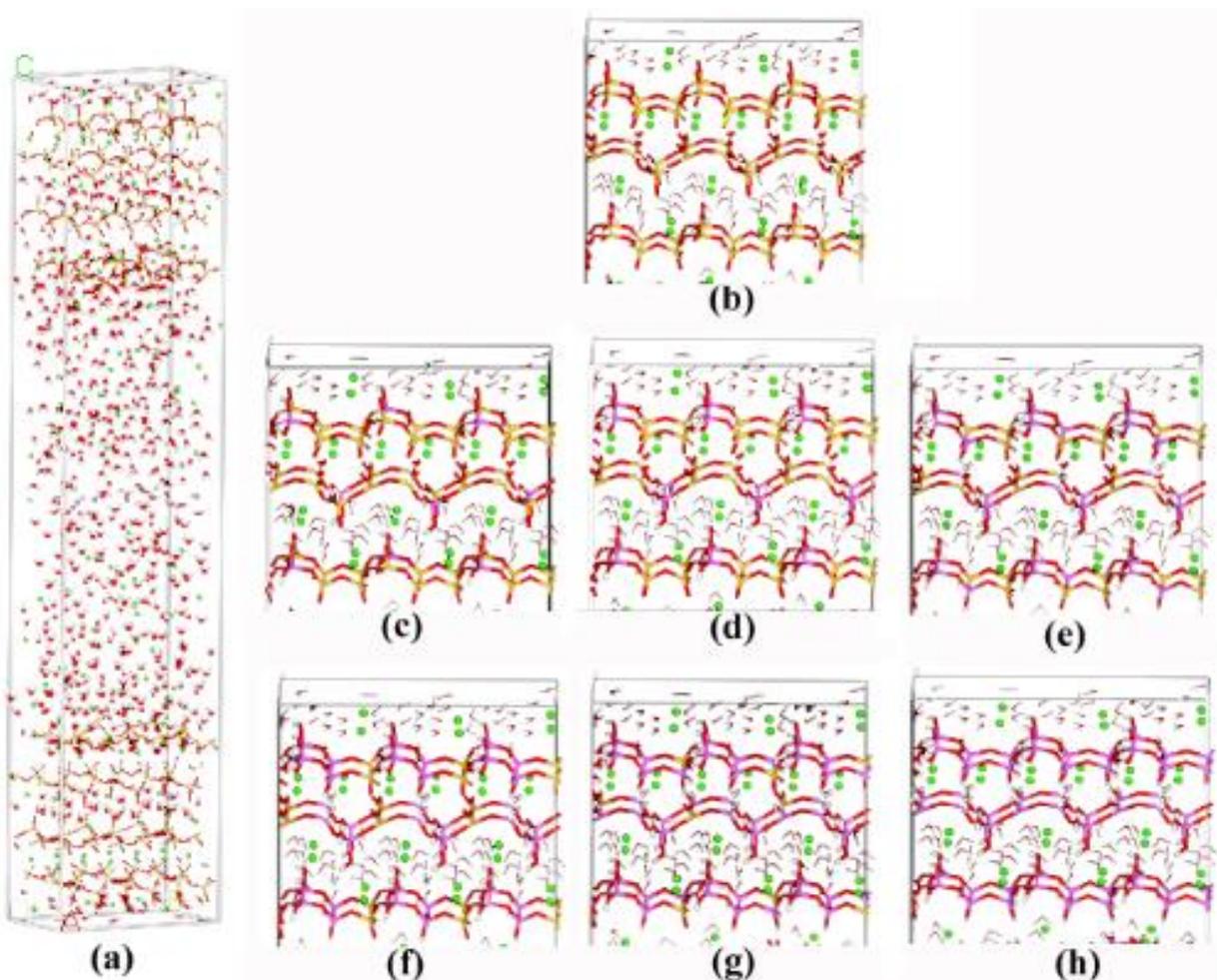


Fig. 2. a) simulation supercell of CSH model; close-view of some tetrahedral chains of: b) CSH model; c) CASH0.2 model; d) CASH0.5 model; e) CASH1.0 model; f) CASH2.0 model; g) CASH5.0 model; h) CAH model. Silicon, Aluminum, oxygen, hydrogen and calcium are shown in yellow, purple, red, white and green colors, respectively

It must be noted that in Figure 2, all of the figures are corresponding to their final configuration after relaxation and obtaining their most stable structure with minimum total energy. The models were equilibrated under NVT canonical ensemble after 300 ps at 300 K that NVT stands for N (number of atoms or molecules in mole), V (volume of supercell) and T (temperature). To perform molecular dynamics analysis Accelrys Materials Studio software (Accelrys, 2012) was implemented. Molecular dynamics simulation was carried out through 2000 ps with a time step of 1 fs. Total simulation time and time step were chosen properly to avoid statistical problems (Hou and Li, 2014).

Every 100 fs, results were extracted so that 20,000 different data sets were stored to be processed.

In this study COMPASS forcefield (Sun, 1998) (Condensed-phase Optimized Molecular Potentials for Atomic Simulation Studies) was used to define potentials between different atoms in one molecule and the atoms in different molecules. This forcefield was chosen because of its great ability to simulate bonds and their potentials in aluminosilicates (Al-Ostaz et al., 2010). Van der Waals interaction was defined by Lenard-Johns 9-6 (LJ 9-6) potential with a cutoff distance, spline width and buffer width of 12.5, 1 and 0.5 Å respectively.

RESULTS AND DISCUSSION

MD-Calculated Diffusion Coefficients of Chloride Ions

Diffusion coefficients of chloride ions in different models are provided in Table 3. It could be found that diffusion coefficient of chloride ions would be decreased by increasing Al/Si ratio. The main reason for better resistance to chloride penetration in C-S-H model with higher aluminum content is its higher chloride binding capacity and Friedel's salt formation consequently. This decreasing trend in the diffusion coefficient of chloride ions for aluminum-included cement pastes is completely consistent with previous experimental findings (Justnes, 1998; Zornoza et al., 2008; Ann et al., 2010; Shekarchi et al., 2010; Ramezaniapour and Jovein, 2012; Zhang and Ye, 2015).

Al/Si Calculation for Experimental Data

Due to lack of information in the literature about MD simulation of aluminum substitution in C-S-H, extracted results in this research were inevitably validated by experimental works on cement pastes. Cement paste includes both crystalline phases such as portlandite, Afm, Aft and the amorphous phase which is C-S-H gel; while in this paper, C-S-H was simulated as main part of cement paste. Nanoscale study of cement paste is particularly faced with simulation and assessment of C-S-H. Because dimensions of most of the other parts of cement paste are related to micro or larger scales (such as portlandite, aggregates, unhydrated cement particles and transition zone) and some of them have very low percentage of the volume of hydrated cement and low impact on cement properties (such as Afm and Aft). Therefore, diffusion coefficient values of chloride ions in C-S-H could not be compared with their values in cement paste.

In this paper, the variation trend of

diffusion coefficients has been compared in C-S-H and cement paste, instead of diffusion coefficient values. The results extracted from C-S-H simulation are comparable with pozzolan-included cement paste results if only all of the aluminum atoms in pozzolanic material incorporated into C-S-H tetrahedral chains and no independent crystalline phase such as Afm and Aft be formed. The main products of pozzolan-included cement pastes with high aluminum content are C-A-S-H and C-A-H. This means that aluminum atoms of these pozzolans would be entered into C-S-H. In this case, the ratio of cement replacement by pozzolan could be converted to aluminum per silicon ratio in tetrahedral chains of C-S-H through a novel technic as follows.

The chemical composition of pozzolans is available using XRF analysis. Aluminum contents of these pozzolanic materials demonstrate by Al_2O_3 oxide percentage. Considering molar mass of Al_2O_3 (101.96 g/mol) and SiO_2 (60.08 g/mol), it is possible to calculate the number of moles of Al_2O_3 and SiO_2 in a specific amount of pozzolan (W) using following equation:

$$\begin{aligned} mol_{Al_2O_3} &= \frac{m_1 \times W}{101.96}, \\ mol_{SiO_2} &= \frac{m_2 \times W}{60.08} \end{aligned} \quad (2)$$

where m_1 and m_2 : are percentages of Al_2O_3 and SiO_2 in pozzolan raw material. Each mole of Al_2O_3 or SiO_2 has 6.022×10^{23} molecules of them (Avogadro's number). Moreover, one molecule of Al_2O_3 has two aluminum atoms and one molecule of SiO_2 has one silicon atom. Therefore, the number of aluminum and silicon atoms in a specific amount of pozzolan could be computed as follow:

$$n_{P,Al} = \frac{2m_1 \times W}{101.96} \times 6.022 \times 10^{23}, \quad (3)$$

$$n_{p,si} = \frac{m_2 \times W}{60.08} \times 6.022 \times 10^{23}$$

Using the above equations Al/(Al+Si) could be easily found:

$$\left(\frac{Al}{Al + Si} \right)_p = \frac{m_1}{m_1 + 0.8485 m_2} \quad (4)$$

If the replacement ratio of cement by pozzolan denotes by R and number of silicon atoms in cement before replacement presented by N, the total number of aluminum

$$\frac{Al}{Si} = \frac{\frac{m_1}{m_1 + 0.8485 m_2} \times R \times N}{N - \frac{m_1}{m_1 + 0.8485 m_2} \times R \times N} = \frac{m_1 R}{m_1 + 0.8485 m_2 - m_1 R} \quad (6)$$

Using proposed method, pozzolan replacement ratio can be conceptually converted to Al/Si ratio assuming that aluminum atoms of pozzolan participated in a hydration reaction to only form C-A-S-H.

Verification

FC3R and MK are two pozzolanic materials with high aluminum content that their main hydration products are C-A-S-H and C-A-H (Payá et al., 2003; Zornoza et al., 2008). This claim could be approximately proved by analyzing thermogravimetric curves produced by previous researchers (Payá et al., 2003). In Figure 3 thermogravimetric analysis curves are shown for 15% replacement of cement by FC3R and MK pozzolans and ordinary cement paste. In this figure, the first and second peaks are related to dehydration of C-S-H and ettringite, respectively; the third peak

and silicon atoms in replaced pozzolan would be calculated by following equations:

$$n_{R,Al} = \frac{m_1}{m_1 + 0.8485 m_2} \times R \times N, \quad (5)$$

$$n_{R,si} = \frac{0.8485 m_2}{m_1 + 0.8485 m_2} \times R \times N$$

Finally, the Al/Si ratio in C-S-H formed by hydration of cement and replaced pozzolan powders together would be equal to:

indicates dehydration of C-A-S-H and C-A-H and last peak corresponds to dehydration of portlandite. It could be found that C-S-H peak in pozzolan-included pastes was smaller with the peak of the ordinary cement paste and C-A-S-H/C-A-H peaks appeared in pozzolan-included pastes. This conclusion could be drawn that most of the aluminum atoms in pozzolans were incorporated in C-S-H and few ettringite crystals has been formed because of adding pozzolans.

Therefore, FC3R and MK are suitable for the sake of aiming the goal of this paper for validation of simulation results and Eq. (6) can be used to find their Al/Si ratio. The chemical composition of FC3R and MK are listed in Table 4 and normalized diffusion coefficient of chloride ions corresponding to different Al/Si ratios are provided in Table 5 for each case.

Table 3. Diffusion coefficients of chloride ions in different simulated models

model	CSH	CASH0.2	CASH0.5	CASH1.0	CASH2.0	CASH5.0	CAH
D ($\times 10^{-10}$ m ² /s)	7.87	6.12	5.85	5.76	5.52	5.32	5.07

Table 4. Chemical composition of FC3R and MK

pozzolan	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Ref.
FC3R	48.2	46.0	0.95	< 0.01	< 0.01	0.50	< 0.01	(Zornoza et al., 2008)
MK	51.85	43.87	0.99	0.2	0.18	0.01	0.12	(Shekarchi et al., 2010)
MK	74.3	17.8	0.82	3.38	0.22	0.00	0.39	(Ramezaniapour and Jovein, 2012)

Table 5. Normalized diffusion coefficient of chloride ions corresponding to different Al/Si, pozzolan to cementitious materials (P/cm) and water to cementitious materials (W/cm) ratios

Method	Pozzolan	P/cm	Al/Si	W/cm				Ref.
				0.3	0.4	0.5	0.7	
Experimental	FC3R	0%	0	1	1	1	1	(Zornoza et al., 2008)
		5%	0.027	0.741	0.804	0.908	0.968	
		10%	0.056	0.652	0.708	0.851	0.814	
		15%	0.086	0.641	0.686	0.794	0.628	
		20%	0.118	0.614	0.703	0.721	0.588	
	MK	0%	0	-	1	-	-	(Shekarchi et al., 2010)
		10%	0.053	-	0.531	-	-	
		0%	0	-	1	1	-	(Ramezaniapour and Jovein, 2012)
		10%	0.023	-	0.778	0.457	-	
		12.5%	0.028	-	0.513	0.367	-	
15%	0.034	-	0.272	0.327	-			
MD simulation			0		1			present study
			0.2		0.78			
			0.5		0.74			
			1		0.73			
			2		0.70			
			5		0.68			
			∞		0.64			

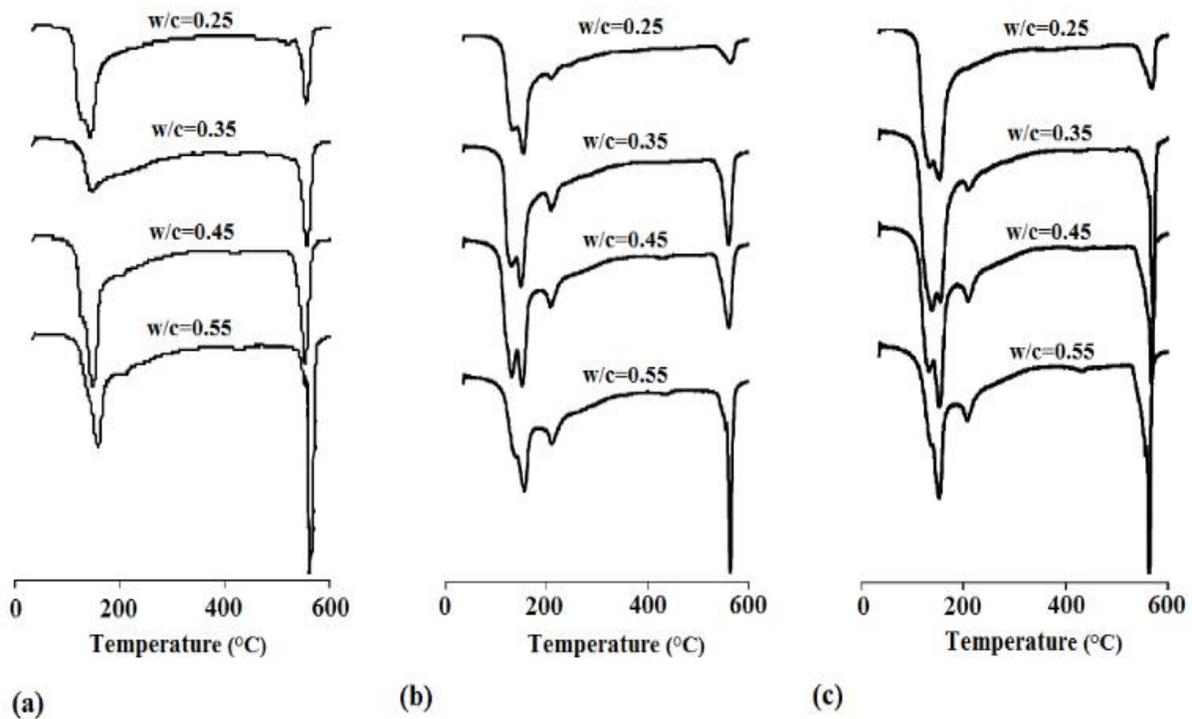


Fig. 3. Thermogravimetric analysis curves in different water to cementitious materials of 0.25, 0.35, 0.45 and 0.55 for: a) ordinary cement paste; b) specimens with 15% FC3R; c) specimens with 15% MK (Payá et al., 2003)

In Figure 4, diffusion coefficient variations versus different Al/Si ratios are shown for present study to be compared with experimental results in the literature. Available Al/Si ratios in experimental researches are limited, while higher values of Al/Si were obtained by simulation in present study. Higher Al/Si ratios may be achievable in the laboratory in future. In this figure calculated diffusion coefficients for lower values of Al/Si were compared with corresponding values in experimental researches.

As it is shown in Figure 4, diffusion coefficients in all cases have been reduced by increasing Al/Si. Reduction rates in experimental cases were larger than simulation case. Diffusion reduction in pozzolan-included cement pastes has two major reasons including porosity reduction

that leads to less permeability; and increasing chloride binding capacity due to C-A-S-H formation. Therefore, lower reduction rate in normalized diffusion coefficients of MD simulated specimens could be because of focusing on C-A-S-H formation only. The other reason of diffusion reduction in pozzolan-included cement pastes (porosity reduction) could not be simulated in nano scale and it needs more study in micro scale to cover all aspects of diffusion regime which is out of the scope of this paper.

Moreover, as it is indicated in Figure 4, the higher the water-to-cement ratio, the lower the rate of reduction of chloride ion diffusion. It can be said that more porosity in samples with a higher water-to-cement ratio has led to fewer effects of adding pozzolan on the closure of pores and reduction of chloride ion diffusion, consequently.

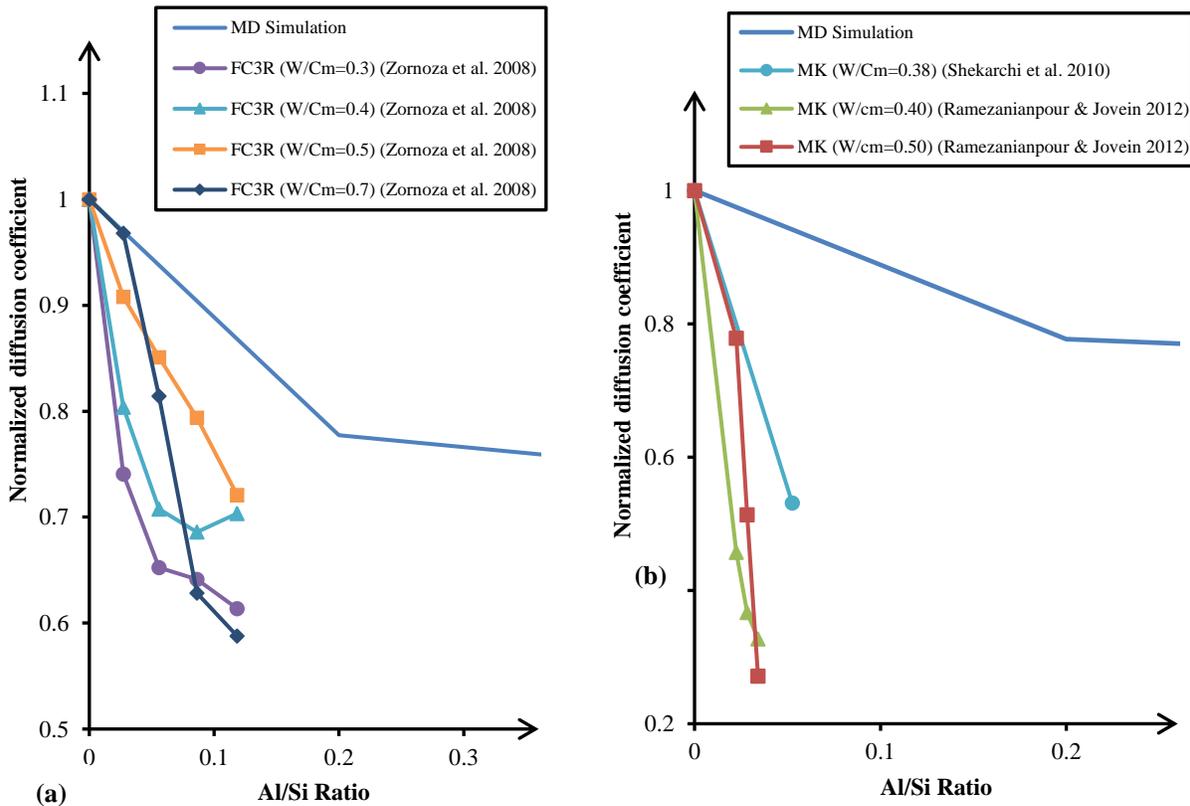


Fig.4. Comparison of normalized diffusion coefficient variation for different Al/Si ratios in C-S-H tetrahedral chains with experimental results for cement pastes including: a) FC3R (Zornoza et al., 2008); b) MK (Shekarchi et al., 2010; Ramezaniapour and Jovein, 2012)

CONCLUSIONS

The aim of this paper was studying the effect of aluminum incorporation in the C-S-H structure on the diffusion coefficients of chloride ions. The silicon substitution by aluminum was considered in bridging and pairing sites in tetrahedral chains of C-S-H in a sense that all of the silicon atoms was substituted by aluminum atoms one by one in different models. Based on the molecular dynamics simulation results, it has been shown that diffusion coefficients of chloride ions would be decreased by increasing aluminum content. Chloride ions diffused into C-A-S-H with a lower rate than C-S-H due to chloride binding in C-A-S-H and formation of Friedel's salt (calcium chloroaluminate hydrates). The higher the aluminum content in the C-A-S-H structure, the more possible it is to form the Friedel's salt. Therefore, more chloride ions would be entrapped by calcium aluminosilicate hydrates and fewer ions might be penetrated.

Moreover, in this paper, a novel method was introduced to convert pozzolan-to-cementitious materials ratio into Al/Si ratio in tetrahedral chains of C-A-S-H. Extracted normalized diffusion coefficients of chloride ions were compared with chloride ion diffusion coefficients in experimental results for pozzolan-included cementitious pastes. All of them showed a decreasing trend for normalized diffusion coefficients by increasing Al/Si ratios. It is worth noting that cement replacement by pozzolans leads to have lower diffusion coefficients of chloride ions. This might be due to less permeability in such cement pastes and chloride binding with C-A-S-H.

Molecular simulation method could evaluate chloride binding with calcium aluminosilicate hydrates. The interactions between all of the cement hydration products could not be described in this method for assessment of cement paste porosity. Because

of ignoring this factor, diffusion coefficients of chloride ions were decreased with a lower rate for MD simulation results comparing with previously-published experimental results, when Al/Si ratio was increased. As the main contribution of this paper, using pozzolans containing higher Al/Si ratios has decreased the corrosion risk.

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