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Research Article

Effect of w/c ratio and cement content on diffusivity of chloride ion in concrete: A molecular dynamics study

Rokonuzzaman Rokon [a] , Md. Shafiqul Islam [a,*] , Nusrat E. Mursalin [b]

[a] Department of Civil Engineering, Rajshahi University of Engineering & Technology, Kazla 6204, Rajshahi, Bangladesh
[b] Department of Civil Engineering, Bangladesh Army University of Engineering & Technology, Qadirabad Cantonment, Natore, Bangladesh

ABSTRACT

When a reinforced structure is exposed to marine environments, chloride-induced corrosion occurs and it decreases the durability and performance of the structure. The degree of humidity, the presence of cracks, environmental conditions, w/c ratio, and cement content are the influencing factors for chloride ion ingress into concrete. All of them, w/c ratio and cement content are treated as the most crucial factors on diffusion. This paper focus on Molecular Dynamics (MD) simulation method to determine the diffusion coefficient of chloride ion in concrete. The effect of w/c ratio and cement content on the diffusivity of chloride ion is also evaluated. The diffusion coefficients are obtained 2.88×10^{-12} m²/s, 3.13×10^{-12} m²/s, and 3.61×10^{-12} m²/s respectively for different w/c ratio of 0.40, 0.45 and 0.50 with constant cement content. Again the diffusion coefficient are calculated 4.6×10^{-12} m²/s, 3.13×10^{-12} m²/s, 2.78×10^{-12} m²/s respectively for different cement content of 300 kg/m³, 350 kg/m³ and 400 kg/m³ with constant w/c ratio. The simulation results clearly indicate that the diffusion coefficient of chlorine was affected by w/c ratio and cement content significantly.

ARTICLE INFO

1. Introduction

Chloride penetration into concrete is of great importance on the durability of reinforced concrete. When a reinforced concrete structure is exposed to marine environments, chloride-induced corrosion takes place and reduces the susceptibility of reinforcement. If a threshold value of chloride content is accumulated with the presence of oxygen or moisture content, the corrosion of reinforcement will initiate (Al-Gadhib, 2010).

A high alkaline environment, which is formed by hydration products of cement, creates a passivated film on the embedded steel surface. So the surface remains chemically stable to protect the steel from corrosion. When a certain amount of chloride content penetrates, it destroys the alkaline environment and disrupts the passivated film (Townsend et al., 1981) and steel surface becomes vulnerable to initiate corrosion.

There are several mechanisms to ingress chlorine through concrete. In all of the mechanisms, it is assumed that diffusion is the most basic phenomenon of chloride ion penetration (Erdoğdu et al., 2004). This diffusion is controlled by some external and internal parameters like the thickness of cover, pore structure, w/c ratio and cement content etc. (Al-Gadhib, 2010). Again initiation of corrosion time is very much dependent on the diffusivity property of concrete.

The service life of a reinforced concrete structure can be reliably predicted by diffusivity of concrete. So the determination of diffusion coefficient of chloride ion is very essential to analyze chloride-induced corrosion initiation time as well as predict the service life of a concrete structure in a marine environment, deicing salts, and coastal areas.

2. Theory

2.1. Chloride penetration

The concentration of chloride at the surface of embedded steel in concrete as well as chloride ion transport can be modeled by Fick's second law of diffusion. It is frequently used in the following form for one-dimension:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

Where C is the total chloride content, t is time and D is the diffusion coefficient. The following boundary conditions are considered:
- a single spatial dimension x, ranging from 0 to 1 for the semi-infinite case,
- $C = C_0$ at $x = 0$ and $t > 0$ (boundary condition),
- $C = 0$ at $x > 0$ and $t = 0$ (initial condition).

where, C_0 is the initial chloride content, x is the distance from edge of the concrete.

An analytical solution of Eq. (1) has the form:

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)\right] \tag{2}$$

where, C_x is the chloride ion concentration at depth x after exposure time t for a surface chloride concentration of C_s at the concrete surface and the expression erf is the Gaussian error function.

The behavior of concentration of chloride ion in concrete structures is adequately described by Eq. (1) and its analytical solution.

2.2. Lennar-Jones pair potential

Any two molecules at a long separation distance attract each other and when come closer repel each other (Hirschfelder et al, 1964). The intermolecular force between chloride ions i and j separated a distance r_{ij} is expressed by Lennard-Jones pair potential as the following equation:

$$U_{ij} = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right] \tag{3}$$

where r_{ij} is the intermolecular distance, U_{ij} is the potential energy, ε is the depth of the LJ potential well, σ is the collision diameter.

In computer simulation, the potential must be truncated at a point named cutoff radius, R_{cut}. If the separation between two molecules becomes greater than the cutoff radius, the intermolecular forces between the molecules will be zero. Actually, the forces exerted between two molecules at a large distance are very small and it can be neglected (Rapaport, 2004) which helps to reduce the computational effort.

$$U_{ij} = \begin{cases} U_{ij} \neq 0, & r_{ij} \leq R_{cut} \\ 0, & r_{ij} > R_{cut} \end{cases} \tag{4}$$

2.3. Theory of molecular dynamics

Molecular Dynamics (MD) is a computer simulation process in which physical movements of particles or atoms are studied. In this method, particles are allowed to interact for a certain period of time, giving a view of the motion of particles (Al-matar et al., 2012)

Molecular dynamics, in its usual form applies numerical integration for Newton's equation of motion (Nissen, 2016).

$$F_i = m\frac{d^2 r}{dt^2} \tag{5}$$

where, F_i is net force on the i-th particle, m is mass and r is the position vector of the i-th particle.

By integrating Newton's equation of motion, new positions and velocities are obtained after time step Δt. One of the most used algorithms is the velocity Verlet algorithm which is used for computing the new positions of molecules.

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{F(t)}{2m}\Delta t^2 \tag{6}$$

where Δt is the time steps in MD simulation.

3. Literature Review

An enormous experimental and numerical study has been seen previously in the determination of the diffusivity of chloride ion through concrete structures based on different parameters and methods. Al-Gadhib (2010) studied the influence of w/c ratio and binder content on chloride ingress in concrete and established a numerical model based on finite element method to predict the diffusion of chloride ion into concrete. Erdoğdu et al. (2004) determined the apparent diffusion coefficient of chloride ion using open-circuit potential measurements and showed the time required to initiate corrosion comparison between synthetic seawater and NaCl solutions exposure.

Wang et al. (2005) proposed a mathematical model for the simulation of electrochemical chloride removal (ECR) process to predict the ionic mass transport associated with chloride ingress into concrete or hydrated cement paste from a saline environment. Li et al. (2015) presented a new transport model to describe the penetration of chlorides in cement-based materials with the concept of double porosity to reflect the influence of pore size distribution on the transport of ionic species in porous materials. Nissen (2016) analyzed the sensitivity of the input parameters in the fib model for chloride ingress and validation of the model for short exposure times. the influences of the meso-structural parameters, including aggregate distribution, aggregate shape, diffu-

sivity properties of the ITZ, water/cement ratio and aggregate content. Du et al. (2014) studied using FEM on the diffusivity of chloride into concrete. Also corrosion rate depends on different w/c ratio presented by Wachira (2019).

In the present study, the transportation of chloride ion into concrete under the atmospheric chloride environment is investigated. Molecular Dynamics method, a widely used plausible simulation method for time dependent response, is carried out to simulate the ingress process. Diffusion coefficient of chlorine ion into concrete is determined to elucidate the chloride transport mechanism. Effects of water-to-cement ratio and cement content on the chloride transport and microstructure are evaluated.

4. Methodology

4.1. Mix proportion

In our simulation, different types of specimen are used which is shown in Table 1. The specimen is considered as crack free and the cement type is Ordinary Portland Cement (OPC).

Table 1. Mix proportion of specimen.

	Simulation ID	w/c ratio	Cement content (kg/m³)
MD simulation with constant cement content	MD1	0.40	
	MD2	0.45	350
	MD3	0.50	
MD simulation with constant w/c ratio	MD4		300
	MD2	0.45	350
	MD5		400

4.2. Simulation geometry

In our MD simulation, we considered a 2D simulation cell with a defined grid size. All parameters of the simulation cell are shown in Table 2. We calculated the total node in our cell 100 which is actually the total number of particles in our simulation. Chloride environment is subjected from one side. The number of chloride ion and oxygen ion are calculated using defined w/c ratio, cement content and which is shown in Table 3.

Table 2. Details of parameters in the MD simulation.

Property	Dimensions
Cell dimensions, μm	15 x 15
Grid size, μm	1.5
No of particles	100
Temperature, K	298
Cutoff radius, μm	3

Table 3. Total number of particles.

Simulation ID	No of Chlorine ion	No of Oxygen ion
MD1	5	95
MD2	6	94
MD3	7	93
MD4	8	92
MD5	6	94
MD6	4	96

4.3. Simulation setting

In this work, the NVE (microcanonical) ensemble was used in a molecular dynamics simulation to equilibrate the total system energy. The time step size was 0.001 s and the total number of simulation cycle was 100. So the total simulation time was 0.1 s. After every 0.01s, all the positions of the particles were saved for further calculations.

At the first of the simulation, we arranged the chloride and oxygen particles in our cell. Initial velocities were generated from Boltzmann's distribution and shifted all velocities that momentum is zero. To adjust kinetic energy to the desired value, we rescaled the resulting velocities. The periodic boundary condition was applied along the *x* and *y* dimensions.

The interactions between Cl-Cl, Cl-O, and O-O were considered and Lennard-Jones pair potential was used to determine the intermolecular forces using Eq. (3). The interaction between the walls and particles was eliminated. Velocity Verlet algorithm was used to integrate Newton's equation of motion using Eq. (6).

After completing the simulation, Mean Square Displacement (MSD) was calculated using the following equation.

$$MSD = \frac{1}{N} \sum_{i=1}^{N} (r(t) - r(t=0))^2 \qquad (7)$$

where, *N* is the total number of particles, $r(t)$ is the position of particles after time t, $r(t = 0)$ is the initial position of the particles.

For further analysis, we plotted the MSD vs time curve in Microsoft EXCEL and the slope of the curve was also determined which is the diffusion coefficient of chloride ion. All MD simulation code was written in FORTRAN 95.

5. Results and Discussion

5.1. Effect of w/c ratio on chloride diffusion

Fig. 1 illustrates the total energy profile of the molecular dynamics simulation at a temperature of 298 K. The total energy is the sum of kinetic energy and potential energy at a certain temperature. From Fig. 1, we can say that total energy and kinetic energy remain steady but potential energy is fluctuating within the simulation. The kinetic energy is positive within a range of 2600 J/mol to 2844 J/mol approximately. The potential energy is both negative and positive within a range of -55 J/mol to 190 J/mol approximately. Therefore, the total energy is the sum of kinetic and potential which comes out to be nearly 2790 J/mol.So, the conservation of total energy verifies that our MD simulation is scientifically plausible and we can use it to calculate the diffusion coefficient of chloride ion.

The Mean Square Displacement (MSD) after every time steps is shown in Table 4 for all MD simulation.
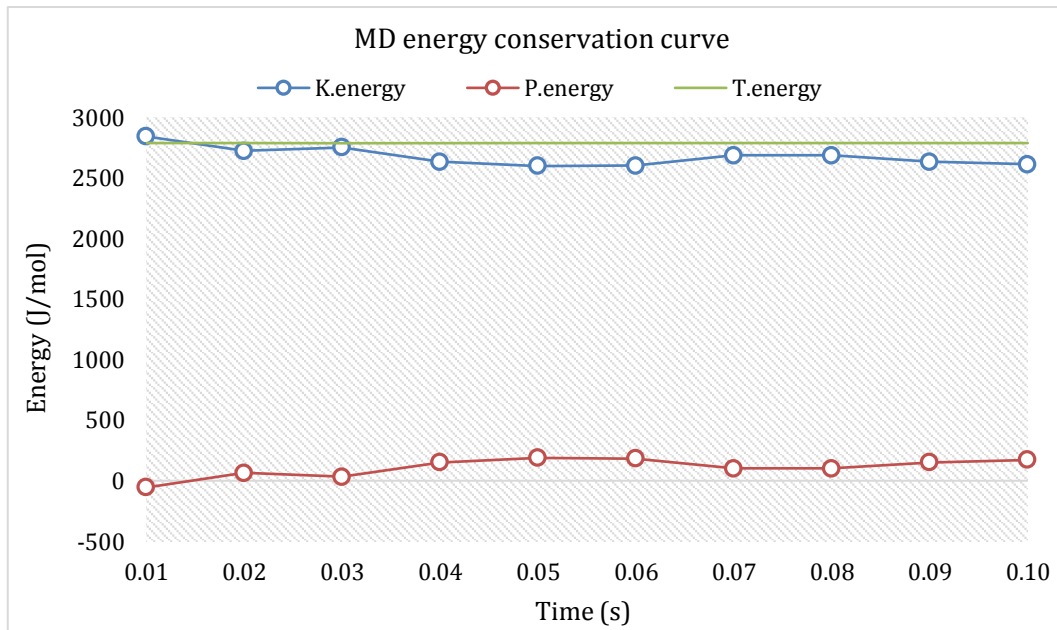

Fig. 1. Total energy conservation within total simulation time.

Table 4. Mean Square Displacement (MSD) with varying time steps.

	MD simulation ID				
Time (s)	MD1 Δr^2 x E-12 (m^2)	MD2 Δr^2 x E-12 (m^2)	MD3 Δr^2 x E-12 (m^2)	MD4 Δr^2 x E-12 (m^2)	MD5 Δr^2 x E-12 (m^2)
.01	0.0042109	0.00421090	0.003699	0.00388257	0.00579376
.02	0.01620982	0.01620982	0.013888	0.01481927	0.02249039
.03	0.03455199	0.03455199	0.027284	0.03158704	0.04766204
.04	0.05942794	0.05942794	0.046844	0.05863773	0.07779074
.05	0.08939900	0.08939900	0.077533	0.09783581	0.11081360
.06	0.12073558	0.12073558	0.117699	0.14484510	0.14225333
.07	0.15468196	0.15468196	0.164876	0.19455749	0.16952453
.08	0.19222454	0.19222454	0.214346	0.25516860	0.19513153
.09	0.23538684	0.23538684	0.26537	0.33342304	0.22046513
.10	0.28534462	0.28534462	0.323554	0.42646436	0.24593148

MSD versus time curves for all simulations are shown in Fig. 2. To calculate the diffusion coefficient of chloride ion accurately, linear regression was used to fit the MSD curve. The slops of the curves which are desired diffusion coefficient are 2.88x10^{-12} m^2/s, 3.13x10^{-12} m^2/s and 3.61x10^{-12} m^2/s for MD1, MD2 and MD3 respectively. It is clearly seen that, as expected, with the increasing of w/c ratio, the higher is the diffusivity of chlorine which is presented in Fig. 3 and thus the chloride movement is faster.
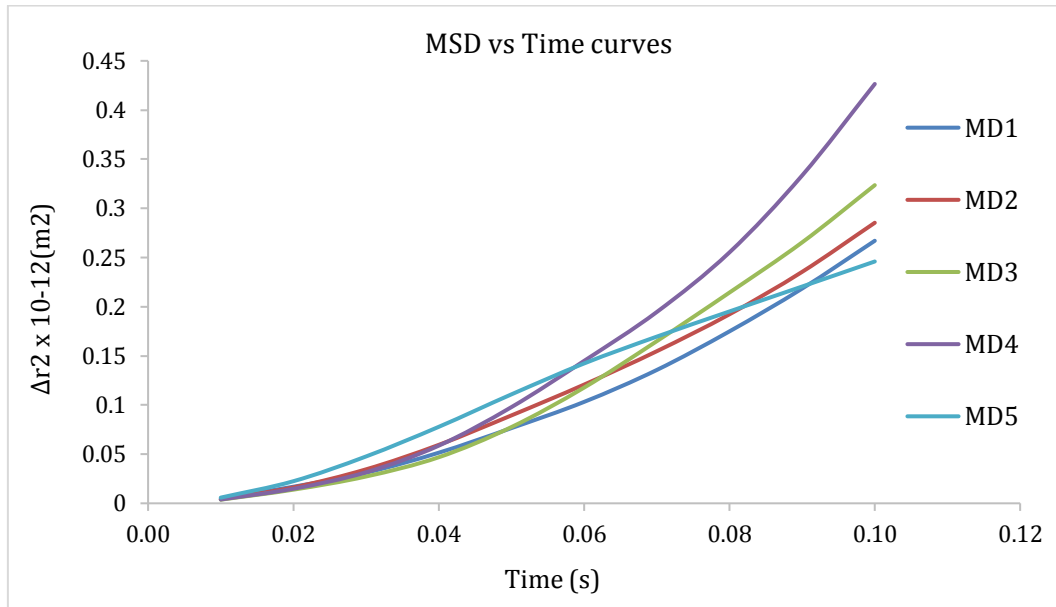
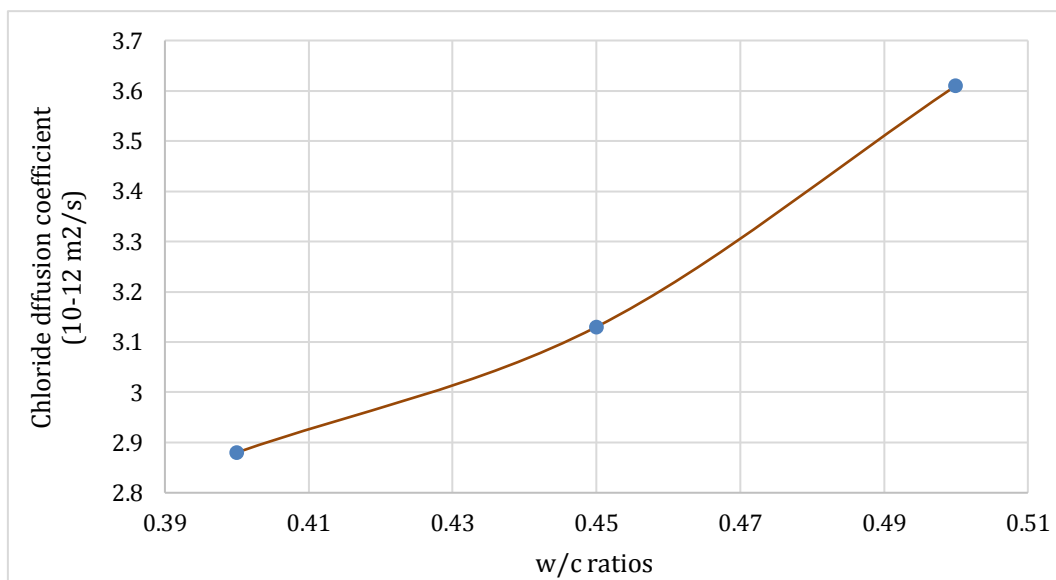**Fig. 2.** MSD vs time curve to obtain diffusion coefficient of chloride ion.

Fig. 3. Chloride diffusion coefficient with different w/c ratios.

5.2. Effect of cement content on chloride diffusion

From MSD versus time curve in Fig. 2, we obtained diffusion coefficient of chloride ion for MD4, MD2, and MD5 are 4.6×10^{-12} m²/s, 3.13×10^{-12} m²/s and 2.78×10^{-12} m²/s, respectively. As expected, the higher the cement content, the diffusion coefficient is lower which is shown in Fig. 4 and thus chloride requires a longer time to reach the same level as that for the lower cement content.

It is clearly seen that the diffusion coefficient of chlorine ion may change significantly with changing of w/c ratio and cement content. With increasing the w/c ratio, chloride diffusivity is also increased. A similar trend is seen for varying cement content in which the lower the cement content, the higher the diffusivity which is more plausible from simulation results.

6. Conclusions

This paper deals with MD simulation to determine the diffusion coefficient of chlorine ion. Again the effect of w/c ratio and cement content on the diffusion coefficient of chloride ion into concrete also evaluated. Then the following conclusions are made:

- With a varying w/c ratio 0.40, 0.45 and 0.50 at a constant cement content, it is evaluated that the diffusion coefficient of chloride ion is increased linearly almost 110% respectively.
- At a constant w/c ratio and cement content varies with 300 kg/m³ to 350 kg/m³, the diffusion coefficient of chloride ion is decreased linearly almost 150%. Again cement content varies with 350 kg/m³ to 400 kg/m³, it is decreased almost 112% .
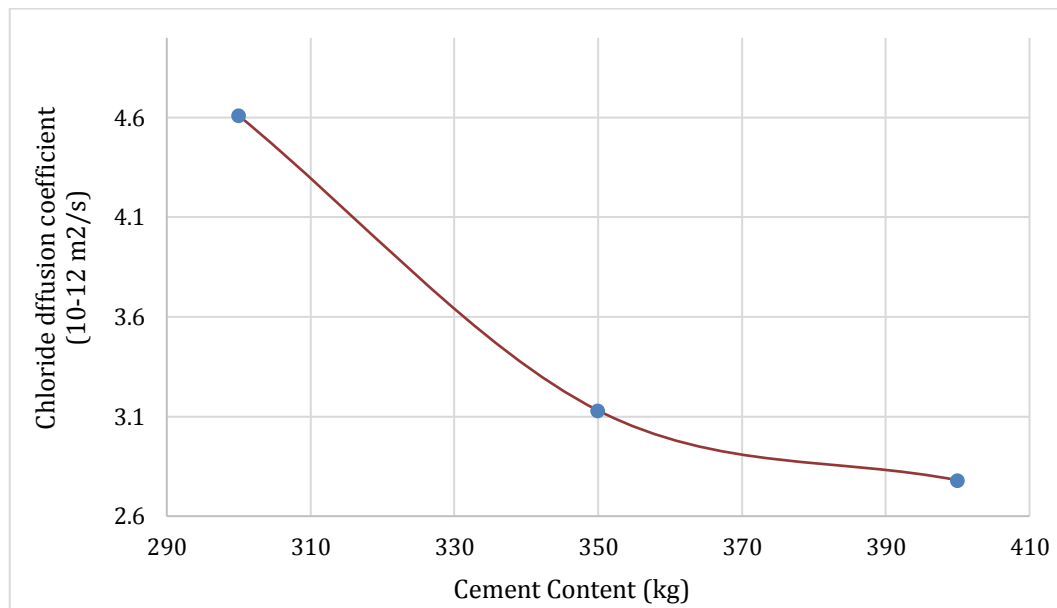
Fig. 4. Chloride diffusion coefficient with different cement content.

Acknowledgements

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