**Impact of water-cement ratio and cement content on pore area percentage and chloride diffusion – A molecular dynamics study**

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**Abstract**

The exposure of a reinforced structure to water-based settings leads to the occurrence of chloride-induced corrosion, resulting in a reduction in both the durability and performance of the structure. The entry of chloride ions into concrete and the pore area percentage is influenced by several elements, including the degree of humidity, the presence of fractures, environmental conditions, water-to-cement ratio (w/c ratio), and cement content. This research focuses on the utilization of the Molecular Dynamics (MD) simulation approach for determining the diffusion coefficient of chloride ions and the pore area percentage within concrete. The evaluation additionally considers the influence of water-to-cement ratio (w/c ratio) and cement concentration on the diffusivity of chloride ions. The diffusion coefficients were determined to be 2.16x10-12 m2/s, 3.62x10-12 m2/s respectively, for varying water-to-cement ratios of 0.40 and 0.50, while keeping the cement content constant. The diffusion coefficients were determined as 2.16x10-12 m2/s, 2.89x10-12m2/s with varying cement content of 350 kg, 300 kg while maintaining a constant water-to-cement ratio. The pore area percentage were calculated 18.7% and 24.5% for varying water-to-cement ratios of 0.40, 0.50 .The pore area percentage were calculated 15.6% and 18.7% with varying cement content of 300 kg/m3, 350 kg/m3 while maintaining a constant water-to-cement ratio .The findings from the simulation demonstrate a clear and significant impact of the water-to-cement ratio (w/c ratio) and cement concentration on the diffusion coefficient of chlorine and pore area percentage.

***Keywords:*** *Chloride, Concrete, W/C ratio, cement content, Diffusion Co-efficient, Pore area percentage ,Molecular dynamics.*

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**Introduction**

Concrete is a basic building material that is widely utilized in construction because of its strength, durability, and adaptability. Cement, water, aggregates, and additional components are combined to make a composite material with a complex microstructure. Enhancing the performance and durability of concrete requires an understanding of its microstructure, namely its porosity and pore area percentage in concrete. The percentage of the entire surface area of concrete that is made up of pores or voids is known as the "pore area percentage" in concrete. [10] Numerous variables, including as the water-to-cement ratio, aggregate characteristics, curing circumstances, varying cement content and mix architecture as a whole, can result in pores. [9] The size, shape, and distribution of these pores inside the concrete matrix might vary. It is crucial to regulate and forecast the macroscopic characteristics of cement-based materials using their pore structure parameters. Understanding the pore area percentage is critical for assessing the porosity of concrete and predicting its performance and durability. The strength, and physical characteristics of the concrete can all also be significantly impacted by these voids. Fractal theory must be applied in order to explain the pore structure of concrete. The fractal dimension of the pore structure was utilized to assess the pore structure characteristics in order to determine the relationship between porosity, shape factor, pore superficial area, average pore diameter, and average diameter and the pore structure features of aerated concrete. [10] Concrete constructions are strong by nature, but with time, they may lose some of their integrity due to continual exposure to the elements. Chloride-induced degradation is one of these risks that should be taken very seriously. The chloride content and penetration depth into concrete are significantly influenced by microclimatic variables, such as the relative humidity at the surface of the material. The quantity of pore water present in concrete has a significant impact on the performance of concrete in real-world conditions and the properties related to the movement of substances in concrete test specimens. The diffusion of ions is limited to the liquid phase that is present within the pore network of concrete. This indicates that the efficiency of ionic diffusion is higher in saturated pores compared to those that are just partially filled with water. The diffusion process in concrete is impeded when there is a drop in water content. This is due to a reduction in the number of porous channels that allow for the continuous flow of pore solution. Consequently, the pathways for ionic diffusion become longer. One possible factor that may contribute to the reduction of ionic diffusion coefficients is the increase in interaction forces between cement paste and ions. This increase in interaction forces can be attributed to the decrease in thickness of the adsorbed water layers. [9] The ingress of chloride ions into concrete plays a significant role in determining the long-term durability of reinforced concrete structures. When a reinforced concrete structure is subjected to maritime environments, the occurrence of chloride-induced corrosion leads to a decrease in the vulnerability of the reinforcement. The initiation of reinforcement corrosion occurs when a certain threshold amount of chloride content is accumulated in the presence of oxygen or moisture [1]. The formation of a passivated coating on the surface of embedded steel is facilitated by the presence of a high alkaline environment, which is generated by the hydration products of cement. The chemical stability of the surface serves to safeguard the steel from corrosion. The infiltration of a specific quantity of chloride content results in the deterioration of the alkaline surroundings and the disruption of the passivated film. Consequently, the steel surface becomes susceptible to the initiation of corrosion. [7] There are numerous ways for chlorine to seep through concrete. It is considered in all the methods that the most fundamental phenomenon of chloride ion penetration is diffusion. [3] Certain internal and external factors, such as the cement content, w/c ratio, pore structure, thickness of the cover, and so forth, regulate its diffusion. [1] Once again, the concrete's diffusivity quality has a significant impact on the onset of corrosion time. The diffusivity of concrete provides a reliable estimate of the service life of a reinforced concrete structure. Determining the diffusion coefficient of chloride ions is therefore crucial for analyzing the initiation time of corrosion caused by chloride and for forecasting the service life of concrete structures in coastal areas, deicing salt environments, and marine environments. [8]

**Model description**

In order to fully understand the diffusion of chloride ions within the concrete structure, a molecular dynamics (MD) study on chloride diffusion and pore area percentage in concrete simulates the movement and interactions of atoms and molecules at the molecular level. A FORTRAN 90 code is created to analyze the chloride diffusion and pore area percentage. The simulation starts by generating a computer model that represents a segment of concrete at the atomic level. The model contains the primary components of concrete, including cementitious particles, aggregates, water, and chloride ions. The replication of the concrete matrix structure and composition is achieved by the use of empirical data and theoretical ideas. Energy calculation parameters, simulation cell parameters, bond lengths, and other relevant force-field parameters that characterize the interactions of each molecular species in the model are used to represent them. Chloride ions are actively added into the system in order to replicate their diffusion process within the concrete structure. The behavior of chloride ions is subject to various factors, including electrostatic interactions with surrounding atoms and molecules, steric effects, water-cement ratio, cement content as well as temperature and pressure. Molecular dynamics (MD) simulations are employed to monitor the temporal trajectory of chloride ions, facilitating the computation of diffusion coefficients and enhancing comprehension of their mobility inside physical structures. Pores or voids are added to the concrete construction to replicate the pore area percentage. These pores, which replicate the porosity present in actual concrete, can have many different kinds of sizes and forms. The porosity influences the mechanical characteristics of the entire structure and makes it possible to evaluate the interactions and permeability of chloride ions in the pores [8].

**Chloride Penetration**

It is possible to model both the chloride concentration at the surface of embedded steel in concrete and the chloride ion transport using Fick's second rule of diffusion. With one-dimension, it is commonly employed as follows:

|  |  |  |
| --- | --- | --- |
|  | $$\frac{∂C}{∂t}=D\frac{∂^{2}C}{∂x^{2}}$$ | (1) |

A total chloride content of C, a time t, and a diffusion coefficient D are represented. Boundary circumstances that are taken into consideration are, An initial condition of C = 0 at x > 0 and t > 0 and a boundary condition of C = Co at x = 0 and t > 0 for the semi-infinite case. A single spatial dimension x, where x ranges from 0 to 1. Where x is the distance from the concrete's edge and Co is the composition of chloride at that point.

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

|  |  |  |
| --- | --- | --- |
|  | $$C\_{x}=C\_{s}[1-erf⁡(\frac{x}{2\sqrt{Dt}})$$ | (2) |

$∁\_{x}$ indicates the chloride ion concentration at depth x after exposure time t for a surface chloride concentration of at$ ∁\_{s}$ the concrete surface, and erf indicates the Gaussian error function.

Eq. (1) and its analytical solution adequately represent the movement of chloride ion concentration in concrete structures.

**Lennar-Jones pair potential**

Any two molecules will attract one another when they are far apart and repel one another when they are near [4]. The Lennard-Jones pair potential expresses the intermolecular force between chloride ions *i* and *j* separated by a distance *rij* as follows:

|  |  |  |
| --- | --- | --- |
|  | $$U\_{x}=4ε\left[\left(\frac{σ}{r\_{ij}}\right)^{12}-\left(\frac{σ}{r\_{ij}}\right)^{6}\right]$$ | (3) |

where σ is the collision diameter, ε is the depth of the LJ potential well, Uij is the potential energy, and rij is the intermolecular distance.

The potential in a computer simulation needs to be terminated at a location known as the cutoff radius, or Rcut. There will be no intermolecular forces between two molecules if their distance from one another exceeds the cutoff radius. In actuality, the forces acting at a great distance between two molecules are negligible and can be disregarded [6], which lessens the computing load.

**Molecular Dynamics**

Molecular Dynamics (MD) refers to a computational simulation technique employed to investigate the dynamic behavior of particles or atoms by modelling their physical movements. In this methodology, particles are let to interact during a designated duration, hence providing an observation of the particle dynamics. According to the study conducted [2]

In its standard form, molecular dynamics uses numerical integration to solve Newton's equation of motion [5]

|  |  |  |
| --- | --- | --- |
|  | $$F\_{i}=m\frac{ⅆ^{2}r}{ⅆt^{2}}$$ | (4) |

where m is the particle's mass, r is its position vector, and Fi is the net force acting on the i-th particle.

After time step Δt, new positions and velocities are produced by integrating Newton's equation of motion. The velocity Verlet algorithm, which is used to calculate molecules' new locations, is one of the most popular algorithms.

|  |  |
| --- | --- |
| $$r\left(t+Δt\right)=2r\left(t\right)-r\left(t-Δt\right)+\frac{F(t)}{2m}Δt^{2}$$ | (5) |

**Pore Area percentage**

The general acceptance of energy conservation and emission reduction policies has led to the increased use of aerated concrete blocks in building engineering. This is mostly owing to its advantageous characteristics such as low density, thermal insulation, acoustic insulation, antiseismic properties, and ease of processing. The influence of the pore structure on the macroscopic properties of aerated concrete blocks has been acknowledged.[9]

To calculate the pore area percentage the following equations are used.

W= W/C ratio x C

Assp= $\frac{V\_{p}}{V\_{bc}}$ $x$ Ass(opc)

Tp = W x Assp

Ts = Tsc –Tp

PAP =$\frac{T\_{p}}{T\_{s}}x100\%$

Here, W is the water content, w/c ratio is the varying water cement ratio, C is the carrying cement content.

Assp indicates the specific surface area of pores which is calculated by bulk volume of concrete (Vbc), 5% volume of pores (Vp) and the specific surface area of OPC (Ass(opc)) which is taken 225m2/kg.

Tp is the total pore area, Ts is the total solid area, Tsc is the total surface area of concrete which is taken 1. Then lastly comes the PAP which is the pore area percentage which is the ratio of total pore area (Tp) and total solid area (Ts).

**METHODOLOGY**

**Mix proportion**

The simulation employs various sorts of specimens, as indicated in Table 1. These specimens are assumed to be free of cracks, and the cement utilized is Ordinary Portland Cement (OPC).

In the conducted molecular dynamics (MD) simulation, a two-dimensional simulation cell was utilized, wherein a specific grid size was defined. Table 2 displays all the parameters pertaining to the simulation cell. The entire number of particles in our simulation was determined by calculating the total node in our cell, which was 100. The chloride environment is being exposed from one side. The quantities of chloride ions and oxygen ions are determined by the utilization of a predetermined water-to-cement ratio and cement content, as indicated in Table 3.

**Table 1: Mix proportion of specimen**

|  |  |  |  |
| --- | --- | --- | --- |
|  | Simulation ID | w/c ratio | Cement content (kg/m3) |
| MD simulation with constant cement content | MD1MD2 | 0.400.50 | 350 |
| MD simulation with constant w/c ratio | MD5MD1 | 0.40 | 300350 |

**Table 2: Details of parameters in the MD simulations**

|  |  |
| --- | --- |
| Property | Dimensions |
| Cell DimensionsGrid size, µmNo of particlesTemperature, KCutoff radius, µm | 15 x 151.51002983 |

**Table 3: Total number of particles**

|  |  |  |
| --- | --- | --- |
| Simulation ID | No of Chlorine ion | No of Oxygen ion |
| MD1 | 5 | 95 |
| MD2 | 7 | 93 |
| MD5 | 5 | 95 |

**Simulation setting**

The NVE (microcanonical) ensemble was employed in this study to conduct a molecular dynamics simulation aimed at achieving energy equilibrium within the entire system. The time step size utilized in the simulation was 0.001 seconds, and the total number of simulation cycles conducted was 100. The overall duration of the simulation was 0.1 seconds. Following each time interval of 0.01 seconds, the locations of all particles were recorded in order to facilitate further calculations. During the initial stage of the simulation, the chloride and oxygen particles were organized within the cell. The initial velocities were derived from Boltzmann's distribution and adjusted such that the total momentum is zero. In order to manipulate the kinetic energy to a specific value, we implemented a rescaling technique on the resultant velocities.

The application of the periodic boundary condition was implemented 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). The following formula was used to get Mean Square Displacement (MSD) once the simulation was finished.

|  |  |  |
| --- | --- | --- |
|  | $MSD=\frac{1}{N}\sum\_{i=1}^{N}\left(r\left(t\right)-r(t=0)\right)$2 | (6) |

where N is the total number of particles, r(t) is the position of the particles after time t, and r (t = 0) is the particles' beginning position. For further study, we plotted the MSD versus time graph in Microsoft EXCEL and determined the slope of the curve, which is the diffusion coefficient of chloride ion. FORTRAN 90 was used to write all of the MD simulation code.

In order to calculate the pore area percentage constant values were taken like bulk volume of concrete = 100, Specific surface area of OPC= 225, Volume of pores 5%, Total surface area of concrete 1. It is given before the position initialization and before the simulation. With the varying w/c ratio and cement content the following formulas area used

W= W/C ratio x C

Assp= $\frac{V\_{p}}{V\_{bc}}$ $x$ Ass(opc)

Tp = W x Assp

Ts = Tsc –Tp

PAP =$\frac{T\_{p}}{T\_{s}}x100\%$

**Results and discussion**

**Effect of W/C ratio on chloride diffusion**

Fig.1, fig.2 and fig.3 represent the kinetic energy, the potential energy and the total energy for every different kind of MD specimen with varying W/C ratio and cement content at a temperature 298K.It shows that for kinetic energy (Fig.1) the highest range is between 2900 j/mol and 2800j/mol and for lowest it almost comes to 2600j/mol. For P.energy in Fig.2 the energy is in both negative and positive range which starts from -55j/mol and goes up to 200j/mol approximately. Therefore, for the total energy sum of kinetic energy and potential energy which varies in different ranges according to the change of the W/C ratio and cement content. As a result, the conservation of total energy confirms the scientific plausibility of our MD simulation and enables us to compute the chloride ion diffusion coefficient.

The figure presented in Figure 4 displays the mean square displacement (MSD) versus time curves for all simulations. In order to accurately determine the diffusion coefficient of chloride ion, a linear regression analysis was performed to fit the MSD curve. The slopes of the curves, which represent the desired diffusion coefficients, were found to be 2.16x10-12 m2/s, 3.62x10-12 m2/s for MD1, MD2, and respectively. It is evident from the results, as anticipated, that an increase in the water-to-cement (w/c) ratio leads to higher diffusivity of chlorine, as depicted in Figure 5. Consequently, the movement of chloride ions is accelerated.

**Table 4: Mean Square Displacement (MSD) for each MD simulation after each time step**

|  |  |  |  |
| --- | --- | --- | --- |
| **Time(s)** | **MD1Δr2 x E-12 (m2)** | **MD2Δr2 x E-12 (m2)** | **MD5Δr2 x E-12 (m2)** |
| .01 | 0.005001682 | 0.003699069 | 0.003699069 |
| .02 | 0.016882898 | 0.01388812 | 0.013888191 |
| .03 | 0.031137244 | 0.027283744 | 0.02728374 |
| .04 | 0.051458754 | 0.046843819 | 0.046843864 |
| .05 | 0.076478399 | 0.077533313 | 0.077580603 |
| .06 | 0.103152984 | 0.117698547 | 0.117698669 |
| .07 | 0.135601357 | 0.164875771 | 0.164876072 |
| .08 | 0.174869824 | 0.214345883 | 0.214346158 |
| .09 | 0.045577738 | 0.265370029 | 0.265370882 |
| .10 | 0.267023948 | 0.323553673 | 0.323554736 |

**Fig. 1. Kinetic Energy comparison curve**

**Fig. 2: Potential Energy comparison curve**

**Fig. 3: Total Energy comparison curve**

***Fig. 4: D. Coefficient Comparison***

***Fig. 5: MSD curve for WC ratio=.5; CC=350; Cls=4.5%***

**Effect of cement content on chloride diffusion**

The diffusion coefficients of chloride ions for MD1, MD5 were determined to be 2.17x10-12 and 2.89x10-12 based on the MSD versus time curve shown in Figure 4. Consistent with expectations, the diffusion coefficient decreases as the cement content increases, as depicted in Figure 4. Consequently, a longer duration is required for chloride ions to reach the same level of concentration as observed in specimens with lower cement content. It is evident that the diffusion coefficient of chloride ions exhibits significant variation in response to changes in the water-to-cement (w/c) ratio and cement content. Specifically, an increase in the w/c ratio leads to an increase in chloride diffusivity. A similar trend is observed when varying the cement content, with lower cement content resulting in higher diffusivity. These findings align well with the simulation results and are more plausible in nature.

**Effect of W/C ratio and cement content on Pore Area Percentage**

As for the pore area percentage when the w/c ratio or the cement content is increased the pore area percentage also increased. For varying w/c ratio the pore area percentage ranges from 18% to almost 25%. Therefore, for varying cement content the pore area percentage ranges from 15% to 22%.

***Fig. 6: Pore Area Percentage curve for varying W/C ratio***

**Fig. 7: Pore Area percentage curve for varying cement content**

**Conclusion**

The purpose of this paper is to determine the diffusion coefficient of chlorine ion and pore area percentage using MD simulation. Again, the influence of the w/c ratio and cement content on the chloride ion diffusion coefficient in concrete is evaluated. Then the subsequent conclusions are drawn:

1.With a varying w/c ratio and constant cement content like .40,.50 it is concluded that in the case of the chloride ion, the diffusion coefficient increases linearly.

2. When the cement content is between 300 and 350 kg/m3, and the w/c ratio remains constant, the diffusion coefficient of chloride ions decreases linearly.

3. With a varying w/c ratio and constant cement content like .40,.and .50 it is concluded that the pore area percentage is also increased .

4.With a varying cement content with constant w/c ratio as 300 kg/m3and 350 kg/m3  it is evaluated that the pore area percentage is also increased.

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